# MANUAL

OF

# ELEMENTARY CHEMISTRY.

A

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OF

# ELEMENTARY CHEMISTRY:

BEING A

## PRACTICAL CLASS-BOOK.

BY

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ILLUSTRATED.

LONDON:

WILLIAM TEGG AND CO., 85, QUEEN STREET,

CHEAPSIDE.

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# PREFACE.

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Many valuable and comprehensive Manuals of Chemistry now exist, but it appeared to the publisher and writer of this work that a Manual might yet find a useful place, which would present a comprehensive view of the more essential facts of Chemistry within a very moderate compass. To effect this, everything like an excrescence has been lopped off. Thus the subjects of Heat, Light, and Electricity, are treated of only in so far as these forces affect chemical action. Animal Chemistry and Organic Chemistry generally are treated more fully than Inorganic Chemistry. A glossary is appended to the work. For some of the microscopic illustrations, the recent work of MM. Robins et Verdeil has been consulted;* and the student desirous of more minute investigation of Animal Chemistry, is recommended to consult that excellent work.

The author begs here to express his thanks to Dr. Cogswell for his valuable assistance.

*London, Dec. 6th,* 1854.

* "Traité d'Anatomie Chimique." Paris : Bailliere, 1853.

# INTRODUCTION.

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IT will be observed that the writer, whilst giving the present views on the constitution of organic bodies, and the doctrine of compound radicals, does by no means positively entertain those views. It is by no means certain, for instance, that alcohol is $C_4H_5O,HO$, or hydrate of the oxide of ethyle. It may be $C_4H_4,2HO$, or $C_4H_6O_2$. Ethyl, or ethyle, $C_4H_5O$, has been obtained, and alcohol can no more be made from it directly than from the direct union of olefiant gas and water. Terms of the same meaning, such as ethyl, ethyle, are used indifferently, with the view of accustoming the Student to regard them as expressing the same meaning. Some writers prefer writing nicotina, others nicotine. If proper rules were laid down and *adhered* to in such cases, it would be better. It is generally understood that the termination in *a* means an alkaloid; in *in* or *ine* a neutral substance; but this rule is seldom adhered to. In the same way, such terms as *sulphuret, sulphide; carburet, carbide,* may be used indifferently.

# TABLE OF CONTENTS.

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## PART I.—GENERALITIES.

## PART II.—ELEMENTARY NON-METALLIC BODIES.

## PART III.—METALS AND THEIR COMPOUNDS.

## PART IV.—ANALYSIS OF MINERAL WATERS.

## PART V.—ORGANIC CHEMISTRY.

# MICROSCOPIC ILLUSTRATIONS.—Plate I.

Fig. 44.

Fig. 43.

Fig. 45.

*b*  *a*  *c*

Fig 46.

*a*  *b*  *d*

*c*
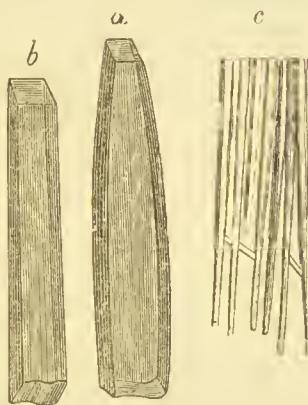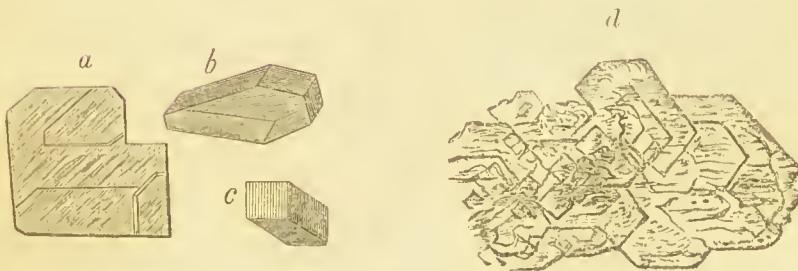
43. Leucine.                    44. Starch.
45. Urea—*a b* in prisms, *c* in needles.
46. Nitrate of Urea—*b c* in prisms, *a d* in plates.

Fig. 47.



Fig. 48.
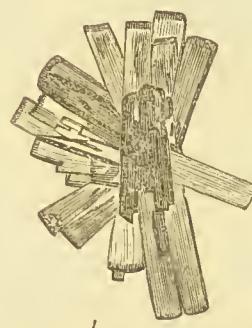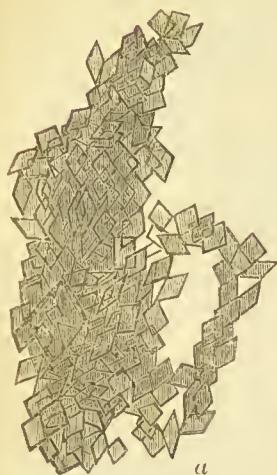
Fig. 49.
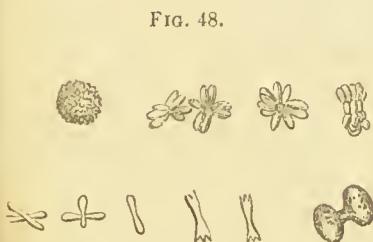
Fig. 50.
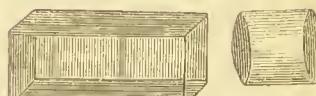


47. Uric Acid—*a* in plates, *b* in prisms, *c* rhomboidal forms.
48. Urate of Soda.                    49. Hippuric Acid.
50. Creatine.

# MICROSCOPIC ILLUSTRATIONS.—Plate III.

Fig. 51.
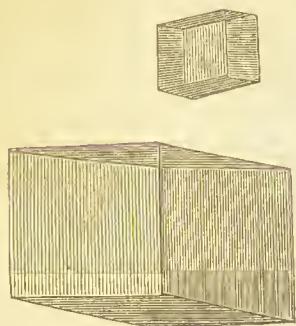
Fig. 52.
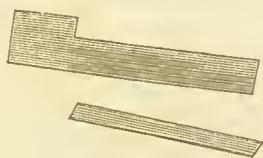
Fig. 53.
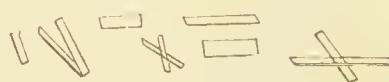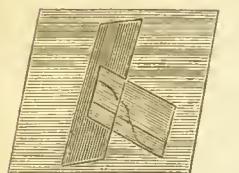
Fig. 54.
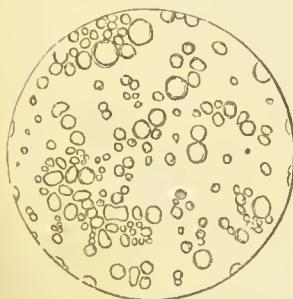
Fig. 55.
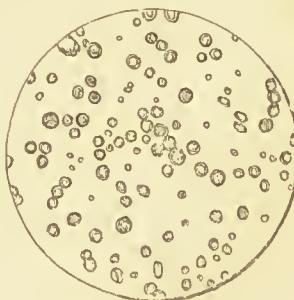
51. Creatinine.

52, 53. Forms of Chloresterine.

54. Milk.

55. Whey.

Fig 56.

Fig. 57.

Fig. 58.

Fig. 59.

*a*  *b*  *c*
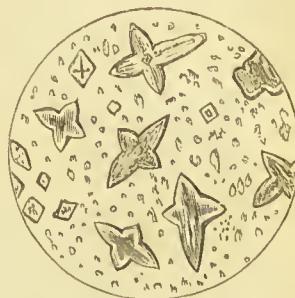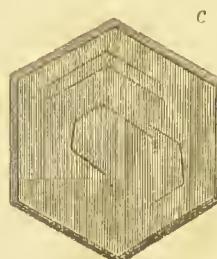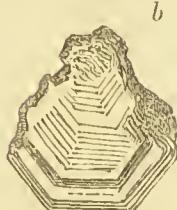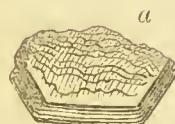
Fig. 60.  Fig 61
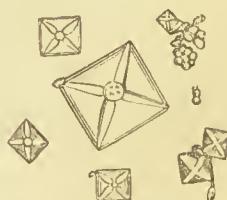
56. Blood globules.  57. Cholate of Soda.
58. Dried Urine.  59. Cystine in various forms, *a*, *b*, *c*.
60. Ammoniaco magnesian phosphate, in dendritic groups.
61. Oxalate of Lime.

Fig. 62.
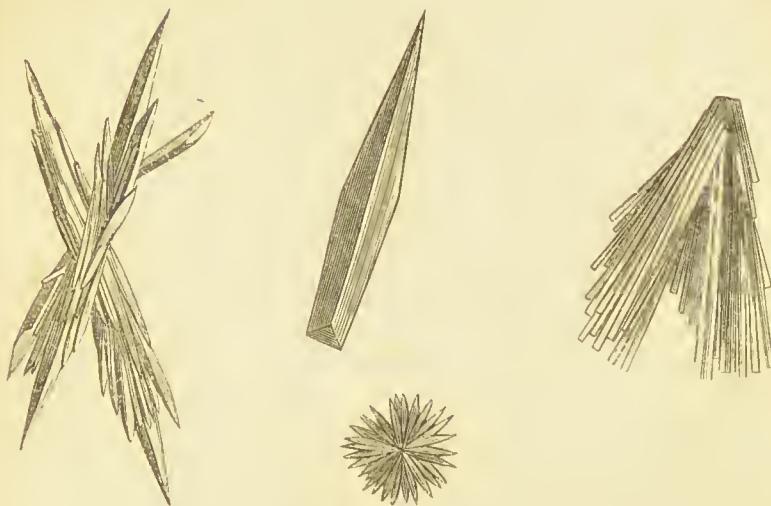


Fig. 63.
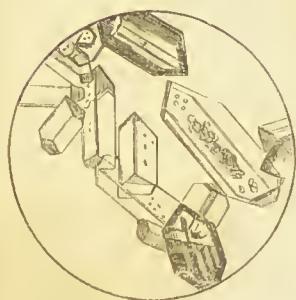
Fig. 64.
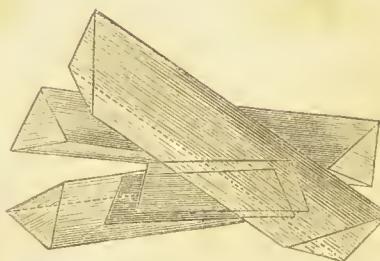


62. Forms of Pneumic Acid.
63. Other forms of ammoniaco magnesian phosphate.
64. Acid phosphate of lime.

# PART I.

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## SECTION I.

### GENERAL DOCTRINES OF CHEMISTRY.

THE term Chemistry does not, like Anatomy, Astronomy, Geology, &c. express or designate the nature of the science. Its etymology has been a subject of dispute—some deriving it from the Greek χυω, to pour; but there can be no reasonable doubt that the real derivation is from Chem, or Chemi, the ancient name of Egypt, where we know that chemistry first attained a degree of excellence. This being the case, the word should be written as above, and not *chymistry*, as is some-times done. In a practical work of this character everything that is not essential must be omitted; nothing, therefore, can be said of the history of the science, it being necessary to pass at once to the description of its principles and laws.

This science, then, deals with those operations and phenomena, whether occurring in nature or produced by art, which are concerned or displayed in the union of two or more dissimilar bodies to form one homogeneous body, or in the separation of one substance or body into others of a different nature. There are two great forms of chemical action: 1st, union, or synthesis; 2nd, separation, decomposition, or analysis. These changes are recognised by concurring changes in the sensible qualities of the substances or bodies concerned. For instance, oxygen and hydrogen unite to form water, which is liquid, while its constituents are aeriform; mercury, a fluid white metal, and oxygen, a gas, unite to form oxide of mercury, a red solid; sulphuric acid, a clear fluid, and copper, form a blue solid; and so forth.

The first consideration to be attended to is, that these combinations are not mere mixtures. When salt or sugar is dissolved in water up to the point of saturation, when the water can take up no more, there is no change in sensible qualities except the solution; but when a mixture of tartaric acid and carbonate of soda is thrown into water, after the effervescence is over, we have no longer the sharp taste of the acid, or the peculiar taste of the soda: the new taste is saline, indicating the change which has taken place. Again, in atmospheric air there is a mere mixture of oxygen and nitrogen gases, arising from what is termed the law of diffusion of gases, by virtue of which gases penetrate each other, and are mutually diffused, in spite of differences of specific gravity. The effect of the addition of nitrogen to oxygen in air is

merely to dilute the oxygen, in so far at least as belongs to the principal chemical processes in which the atmosphere is concerned, such as combustion and respiration; but when two gases, such as nitric oxide and oxygen, come together, we instantly see a change; deep red fumes are formed, and we know that there is chemical combination. In every instance these changes are not visible at first to the senses; but they are evident on a more minute investigation. Carbonic acid and oxygen are apparently similar, but when they are weighed their specific gravities are different; and a candle will be extinguished in the former, but will burn in the latter. Changes then produced by chemical action are accompanied by changes in the sensible qualities of bodies.

The great difference between chemical union and the mere mixture of bodies is, that the former takes place in certain definite proportions. It is not any quantity of one body that will chemically unite with any quantity of another. Not that one part, by weight, of hydrogen gas will unite with ten, or fifteen, or twenty parts of oxygen gas; but, it is found by experience, that one part of hydrogen gas will unite with eight parts of oxygen to form water; or with twice that, or perhaps thrice that, to form other compounds. Or again, fourteen parts of nitrogen gas will unite with eight parts of oxygen to form one compound, with sixteen parts to form another, with twenty-four parts to form a third, with thirty-two parts to form a fourth, and with forty parts to form a fifth. These substances, so formed, are the series known as the protoxide, deutoxide, teroxide, and peroxide of nitrogen or azote; and the last is the body termed nitric acid commonly known as *aqua fortis*. But atmospheric air, which has been called a mere mixture, contains twenty-three parts by weight of oxygen to seventy-seven of nitrogen, as nearly as possible,—proportions · in which the harmony that prevails in the true chemical combinations of oxygen and nitrogen can no longer be traced. It is such an act of combination as that in which the component parts are united in definite proportions, that is termed a true chemical phenomenon. The substance so formed is a compound, the substances united to form it are its elements, and the result is said to be brought about by chemical affinity. But a force must have been exerted to draw these elements together, and that is termed chemical attraction. When Newton discovered the law of gravity, he merely stated a fact, viz.—That substances gravitated towards each other according to a certain rate; when he went beyond this and spoke of an attractive force he enunciated a hypothesis: of the facts of gravitation, and the laws according to which these facts may be classed, we have proof; but that these are the results of an attractive force, is a creation of the mind alone. The idea of this force exists in the mind alone, and may or not exist in the external world. When a spark explodes gunpowder, all that are seen are the spark, the gunpowder, and the explosion; but when we begin to reflect on what has taken place, the mind is irresistibly led to the conclusion, that there must have been an adaptation on the part of the spark to explode the gunpowder.

Now, by the term chemical affinity is expressed a fact, that some

bodies have a tendency to unite with other bodies—a fact cognisable by the senses; when it is said that this is owing to an attractive force, that is a theory, or a hypothesis, but one which the mind cannot help believing.

In chemical phenomena this force acts only at insensible distances, that is to say, the bodies possessed of different properties to be drawn together, and forced into a homogeneous one, must be, as far as our senses can estimate, in contact. The particles of the one must be mingled intimately with the particles of the other.

Those bodies in whom no constituents have yet been discovered are termed elementary. There is no reason for this name, except the fact, that as yet they have not been resolved into any elements ; but the ancients termed water an element, and it is now known to be a compound of oxygen and hydrogen. The fixed alkalies as they were called, were supposed to be elements, until the genius of Davy, making use of a newly-invented power, that of galvanism, tore their elements asunder, and shewed that such bodies as caustic potass and soda were compounds of metals, called potassium and sodium, with oxygen ; and there can be no doubt that some of those bodies which are now called elementary are really compound. But, in a work like this, science must be treated on the basis on which it at present exists.

Bodies resulting from the union of two simple substances are termed compounds of the first order ; such, for instance, is water, formed by one equivalent of oxygen and one of hydrogen ; as sulphuric acid, a compound of one of sulphur and three equivalents of oxygen ; or caustic soda, of one of the metal sodium and one of oxygen ; and, such bodies are often capable of combining with each other and forming other compounds, which are termed of the second order. Such for instance are the neutral salts ; for instance, sulphuric acid and soda form sulphate of soda ; and these compounds of the second order are generally capable of uniting and forming compounds termed of the third order. In compounds of the second order a distinction may be drawn between *proximate* and *ultimate* elements; for instance, in sulphate of soda, sulphuric acid and soda are the proximate elements, oxygen, sodium (the metallic base of soda), and sulphur the ultimate. In compounds of the third order we may speak of their elements of the second order, of the first order, and their ultimate elements.

When one simple or compound substance brought in contact with another body of a compound nature decomposes the latter and unites with one of its component parts, which is taken from the other constituents, so that a new body is formed, and one or more of the constituents expelled or isolated, it is said to be owing to a stronger affinity on the part of the body introduced for the constituent which it combines with, than is entertained on the part of the latter for what is expelled or isolated. Thus, when nitrate of potass, a compound of nitric acid and potass is acted on by sulphuric acid assisted by heat, the nitric acid is expelled from the potass, and driven off. Then it is said, that the sulphuric acid has a stronger affinity for the potass than the nitric acid.

Here an important accompanying condition generally prevails, viz.—
that when three bodies are brought in contact, the general tendency is
for that body whose removal is most favoured by the circumstances in
which the three are placed to be expelled or·separated, and the other
two to unite. Thus, in the case quoted, the nitric acid is more volatile
than the sulphuric, and it is removed, the decomposition being
assisted by the operation of heat, whereby the gaseous nitric acid is
expelled,* and the potass and sulphuric acid combine. When a similar
decomposition is effected in water, generally the tendency is for the
compound most insoluble to be formed; and the constituent having
least tendency to form an insoluble compound, in such a case, to be
separated in the water. Thus, when tartaric acid is added to many
compounds of potass with acids, it separates the potass as a base from
the acids, and forms the insoluble bitartrate of potass. Muriatic acid,
in like manner, separates most acids from their compounds with silver,
forming the insoluble chloride of silver.

The same circumstances are observed in what are termed double
decompositions, viz., where two compound bodies mutually decompose
each other, where there are four principles concerned in the process,
and two new compounds are formed. Thus, when carbonate of lime and
muriate of ammonia are heated together, the two most fixed and volatile
substances possible in the case are formed : viz., carbonate of ammonia,
the more volatile ; and muriate of lime, the more fixed. Here the heat
determines the decomposition. Again, when carbonate of soda and
muriate of baryta are joined with water, the most insoluble and soluble
bodies that can be formed out of the four proximate elements, viz.,
carbonic acid, soda, baryta, muriatic acid—that is to say, carbonate of
baryta and muriate of lime are formed. Thus, whatever may be the
natural affinities of different bodies for each other, these and similar
circumstances seem to prove that the affinities are powerfully influenced
by the circumstances under which they are called into play.†

* Potass and lime with the aid of heat drive off ammonia from its acids.
† Berthollet maintained that in this way nearly all decompositions
were to be explained; thus, when nitrate of potass and sulphuric acid are
mixed, it is not the superior affinity of the sulphuric acid for the potass
which determines the formation of sulphate of potass and evolution of
nitric acid, but the volatility of the nitric; in like manner, when muriatic
acid decomposes the nitrate of silver, the result is determined by the insolu-
bility of the chloride of silver. He gives an explanation, however, of the
facts, which seems too narrow. When the sulphuric acid is added to
nitrate of potass, he makes out that the sulphuric halves the potass with
the nitric in this way:—take 8 atoms of sulphuric acid and add it to 8
atoms of the nitrate of potass, and there will be formed 4 of nitrate and
4 of sulphate of potass, 4 of free nitric, and 4 of free sulphuric acid
remaining; but the application of heat drives off the nitric, and the
4 free sulphuric remaining unbalanced by the nitric, it attacks the four
remaining equivalents of the nitrate and halves them, and heat drives
off other two of the nitric ; he gives a similar explanation of those
cases where the volatility or insolubility of some of the compounds

Again, some substances will combine on coming into contact with each other; thus, when metallic antimony in powder is put into chlorine it takes fire, and the chloride or butter of antimony is formed; but when sulphur and copper are put together they will remain for some time without action; but on the application of heat they take fire and form the sulphuret of copper. Hydrogen and oxygen may be mixed together, without change: but, on the application of heat, or the introduction of spongy platinum, or passage of electricity through the mixed gases, they combine and form water. Again, masses of different bodies require to be broken down, and thoroughly mixed or dissolved before they will unite. The rays of light will decompose chloride of silver, as evidenced by its blackening, and a mixture of chlorine and water is caused to undergo several chemical changes through their action; hence light has the power of effecting chemical changes. Then the substances, called ferments, possess the power of occasioning chemical changes in other bodies, through an action little understood. Lastly, many chemical phenomena take place in the living body in a manner that cannot be understood by the ordinary laws of the science, and compounds are formed which cannot be imitated in the laboratory. By way, therefore, of classifying some of these chemical phenomena, whose mode of production we cannot in all cases understand, we may say, that the laws of chemical affinity are modified or controlled by the forces of—1, cohesion; 2, gravitation; 3, heat; 4, light; 5, electricity; 6, catalysis; 7, vitality; to which others of less importance may be added. The mode in which these forces operate on chemical affinity is to be afterwards considered.

The fact that bodies combine in certain definite proportions is generally termed the atomic theory, or doctrine of chemical equivalents; the latter phrase expresses a fact, the former a theory, however probable. It is a fact that bodies do combine in certain definite proportions; but that they do so because their ultimate particles or atoms are of different sizes, is an inference which only amounts to a hypothesis which very plausibly explains the fact.

Connected with the doctrine of chemical equivalents is another very important fact, viz., that gases generally combine in equal volumes, or multiples or sub-multiples of them. For instance, a pint of chlorine will combine with a pint of hydrogen to form muriatic acid; a pint of nitrogen will combine with three pints of hydrogen to form ammonia; or, a half-pint of oxygen will unite with a pint of hydrogen to form water; or a pint of oxygen with a pint of the latter to form the peroxide of hydrogen.

With regard to the doctrine of atomic weights or equivalents by

that can be formed favours the decomposition. But how explain so easily other facts, as the decomposition of steam by iron at a red heat, the formation of the oxide of iron, and evolution of hydrogen, and the reduction of this same iron to the metallic form by heating it with hydrogen? It appears, in fact, that in chemical action there is always a tendency to change, and that, *cæteris paribus*, when a change can take place it does so.

volumes, various hypothetical views have led to differences of opinion concerning the standards of comparison to be fixed upon. Thus, hydrogen has the lowest chemical equivalent of all bodies; it combines with others in the smallest proportions by weight, hence it seems properly fixed upon as the standard of comparison; and this is especially strengthened by a very probable hypothesis of Dr. Prout, viz., that the combining equivalents of all bodies are multiples of hydrogen by a whole number, so that, if this view were correct, by estimating hydrogen as one, we should have all other bodies, simple and compound, multiples of this: that is to say, in our calculations we should avoid fractions, which would be very convenient. It is certainly not true, as far as the results of experiment have gone, that the atomic weights of all bodies are multiples of hydrogen by a whole number; nevertheless, there is a strong general impression among scientific men that Prout's theory has a strong basis of truth, and that the exceptions which exist to it are only apparent, and would disappear on a closer examination. Thus carbon some years ago was supposed to have a chemical equivalent of 6.05 to hydrogen as 1. Very accurate experiments by Dumas seemed to prove it to be exactly 6; but Liebig has since made it to be 6.088. It is clear that we might make use of any standard we chose, call hydrogen 100, or oxygen 100, as is done by Berzelius, or 1, as by others; but the general practice is to take hydrogen as 1, and oxygen as 8, and estimate other bodies accordingly.

Now, gaseous bodies combine with each other, as a general rule, in equal volumes, or multiples of volume; hence, as a pint of hydrogen combines with a pint of chlorine to form muriatic acid, and we know that by weight nearly 36 parts of chlorine must combine with one of hydrogen, it follows that chlorine must be 36 times as heavy as hydrogen; hence, if we know the specific gravity of hydrogen, $i. e.$, its relation in weight to atmospheric air, which is taken as the standard of sp. gr. of gases, as water is of fluids and solids; then, by multiplying the sp. gr. of hydrogen by 36 we should get the sp. gr. of chlorine, which is the case. Hence, if all bodies in the gaseous form combined in equal volumes, then their relation to each other by weight would be as their atomic weight or chemical equivalents. But if we fix upon hydrogen as the standard in volume, as we have done in atomic weight, then only $\frac{1}{2}$ its volume of oxygen will combine with it to form water; and if this $\frac{1}{2}$ weighs 8, and the 1 of hydrogen only 1, then it is clear that oxygen is 16 times heavier than hydrogen: this is not confined to oxygen; 1 volume of hydrogen, weighing 1, will combine with $\frac{1}{6}$th of sulphur vapour, weighing 16, to form sulphuretted hydrogen, so that the sp. gr. of sulphur vapour must be $16 \times 6 = 96$, to hydrogen as 1. It is found more convenient to consider hydrogen the standard of volume, and call it 1.

From these facts, the mode of determining the sp. gr. of compound gases by theory may be elucidated. This sp. gr. will depend on the amount of condensation which the constituents undergo when they unite. Thus 1 eq. of hydrogen unites with 1 eq. of chlorine to form 1 eq. of muriatic acid gas, and there is no condensation. The

sp. gr. of muriatic acid gas, therefore, is found by adding that of chlorine to hydrogen, and dividing by 2. The formula in such cases, when A and B unite to form C, for finding the sp. gr. would be—sp. gr. A + sp. gr. B, divided by 2 = sp. gr. C. When one of carbon vapour unites with one oxygen to form carbonic acid, since the whole of the oxygen is condensed into the carbon vapour, the formula is sp. gr. A + sp. gr. B = sp. gr. C.

Certain theoretical opinions are entertained with regard to the atomic theory which the student should be aware of, although it may not be expedient at first to take up much space with their description.

As the atomic theory itself rests only on a probable hypothesis, so the conclusion that compound bodies contain certain definite proportions of their elements, to be represented as 1 of one element to 2 of the other, or *vice versa*, is a hypothesis to be supported by other probable circumstances. In water we find 8 parts of oxygen, by weight, combined with 1 of hydrogen; but 2 volumes of hydrogen unite with 1 of oxygen ; and Berzelius has laid down as a law, which many consider extremely probable, that equal volumes of substances in the gaseous state contain equal atoms. According to this view, therefore, 2 atoms of hydrogen would combine with 1 atom of oxygen ; and as the proportion of oxygen by weight is 8 to 1, it follows that the 2 atoms of hydrogen weigh each only $\frac{1}{2}$ ; or, if we make the atomic weight of hydrogen 1, as on the ordinary scale, then oxygen must be 16. In the same way, all the substances that combine with oxygen in multiples of its volume, must undergo a reduction in their atomic weight, or that of oxygen be raised.

The fixing of atomic numbers is partly regulated by analogy. Having fixed upon the proportion of A which unites with B to form a compound C, and the proportions in which C unites with D, an idea is gradually formed as to what is the lowest combining number that can be conveniently fixed upon for an element, or compound. The law of volumes favours materially this calculation, in regard to the substances which are gaseous. In regard to other compound bodies, the strongest oxide of a metal is regarded as that which contains the metal and oxygen in single equivalents. There are two oxides of mercury, the red and the black ; the former contains 100.7 of mercury, with 8 of oxygen ; if it be considered the stronger base, then the combining eq. of mercury is 100.7 ; if the black oxide is regarded as the base, it contains 100.7 to 4 of oxygen ; and if we have already determined that oxygen is to be 8, then mercury must be 201.4, and the red oxide must be called the peroxide, the black oxide the protoxide. But if we prefer the red oxide, or peroxide, as the base—if we think it forms the most stable compounds with acids—then it is the oxide, or protoxide, and the other the suboxide. It is in this way that corrosive sublimate — analogous to the red oxide, but containing chlorine united with mercury instead of oxygen—was at one time called the bichloride, and calomel, analogous to the black oxide, called the chloride ; whereas we now call the former the chloride, and the latter

the subchloride. According to the former supposition, the combining eq. of mercury is 201.4 ; according to the latter, 100.7.

Again ; bodies very closely analogous, chemically and physically, are supposed to form compounds in similar proportions with other bodies. A common illustration is from such cases as nickel and cobalt ; if the former combine with oxygen in the proportions of 1 : 1 and 2 : 3, this will likely be the case with the other.

When the composition of a body is known by weight, or, if a gas, by weight and measure, the question then is, to fix upon the proportions of equivalents of the elements, each by analogy, or thus to determine the equivalent of either of the bodies, supposing that not to be already decided.

## SECTION II.

### CHEMICAL NOTATION AND FORMULAS.

THE necessity of a chemical nomenclature to express facts in a brief and clear manner, where decompositions are concerned, soon became apparent. Such a nomenclature now exists. Without it there would be very great difficulty in making the student understand many processes.

The mode in which this is effected is as follows. In the first place the various elementary bodies have symbols of a very simple character, formed by taking the initial of their names ; and, in cases where the names of two or more elements are the same, taking some other letter of the name for distinction.

Here is a list of the names of the various elements, with their symbols, and atomic weights or equivalents, as recognised at present, on the assumption of the atomic weight of hydrogen being 1.

| Name of Element. | Symbol. | Equivalent. |
|---|---|---|
| Aluminum | Al. | 13.69 |
| Antimony, or Stibium | Sb. | 129.03 |
| Arsenic | As. | 75.00 |
| Barium | Ba. | 68.64 |
| Bismuth | Bi. | 70.95 |
| Boron | B. | 10.90 |
| Bromine | Br. | 78.26 |
| Cadmium | Cd. | 55.74 |
| Calcium | Ca. | 20.00 |
| Carbon | C. | 6.00 |
| Cerium | Ce. | 46.00 |
| Chlorine | Cl. | 35.50 |
| Chromium | Cr. | 28.15 |
| Cobalt | Co. | 29.52 |
| Copper | Cu. | 31.66 |
| Didymium | D | |
| Fluorine | F. | 18.70 |
| Glucinum | Gl. | 26.50 |
| Gold (Aurum) | Au. | 98.33 |

| Name of Element. | Symbol. | Equivalent. |
|---|---|---|
| Hydrogen | H. | 1.00 |
| Ilmenium | Il. | |
| Iodine | I. | 126.36 |
| Iridium | Ir. | 98.68 |
| Iron (Ferrum) | Fe. | 28.00 |
| Lanthanum | La. | 48.00 |
| Lead (Plumbum) | Pb. | 103.56 |
| Magnesium | Mg. | 12.67 |
| Lithium | Li. | 6.43 |
| Manganese | Mn. | 27.67 |
| Mercury (Hydrargyrum) | Hg. | 100.70 |
| Molybdenum | Mo. | 47.88 |
| Nickel | Ni. | 29.57 |
| Niobium | | |
| Nitrogen, or Azote | N. or Az. | 14.00 |
| Osmium | Os. | 99.56 |
| Oxygen | O. | 8.00 |
| Palladium | Pd. | 53.27 |
| Pelopium | Pe. | |
| Phosphorus | Ph. | 32.02 |
| Platinum | Pt. | 98.68 |
| Potassium (Kalium) | K. | 39.00 |
| Rhodium | R. | 52.11 |
| Ruthenium | Ru. | 52.11 |
| Selenium | Se. | 39.57 |
| Silicon | Si. | 21.35 |
| Silver (Argentum) | Ag. | 108.00 |
| Sodium (Natrium) | Na. | 22.97 |
| Strontium | Sr. | 43.84 |
| Sulphur | S. | 16.00 |
| Tantalum, or Columbium | Ta. | 92.30 |
| Tellurium | Te. | 66.14 |
| Terbium | Tb. | |
| Thorium | Th. | 59.59 |
| Tin (Stannum) | Sn. | 58.82 |
| Titanium | Ti. | 24.29 |
| Tangeten, or Wolfram | W. | 94.64 |
| Uranium | U. | 60.00 |
| Vanadium | V. | 68.55 |
| Yttrium | Y. | 32.20 |
| Zinc | Zn. | 32.52 |
| Zirconium | Zr. | 33.62 |

Besides these symbols of a simple character, others are in use for compound bodies, which are very prominent and often alluded to, to save space, such as Aq. for Water; Cyanogen, Cy.; Acetic acid, $\bar{A}$; Morphia, $\overset{+}{M}$.

The general mode is to express the base or electro-positive element first. Thus, water is written HO; potassa, or the oxide of potassium, KO; or, sometimes, the equivalent of oxygen is put above the symbol of the electro-positive element in the form of a dot; thus water is sometimes written $\overset{\cdot}{H}$; carbonic acid, a compound of one eq. carbon

with two of oxygen, $\ddot{C}$, instead of $CO_2$; sometimes the figure in such a ease is written above, as $CO^2$; but here the former mode will be preferred.   The symbols for sulphur are sometimes abbreviated in the same way; thus the tersulphuret of a metal compound of one eq. of the metal, and 3 eqs. of sulphur is sometimes written, instead of $MS_3$, $\dddot{M}$.   In short, there are various modes of writiug these symbols, but the preferable modes seem .—

1. To write the number of the equivalents of the elements of a compound below each element.

2. To employ ueither comma nor other sign, except when some-thing is meant; for instanee, $KOSO_3$ would mean sulphate of potass; but $C_2H$, $Cl_3$ would mean that the comma shews that the $C_2H$, or *formyl*, is combiued with the $Cl_3$ in chloroform, as a compound base.* Again, the sign $+$ is often used to deuote eombination; it would be better restricted to signify separation for a time, addition merely until a chemical deeompositiou is accomplished.   Thus, $NaO\,SO_3 + BaOClH$. would mean that an equivalent of the sulphate of soda, and one of the muriate of baryta were added together; aud the results the formation of sulphate of baryta and muriate  of soda would be expressed by the  following equation, $NaO\,SO_3 + BaOClH = NaOClH + BaO\,SO_3$.

3. In eases where a double salt is formed, the use of the eomma also  is advantageous; thus, $FeO\,SO_3$, $KOSO_3$ indicates that a double salt of sulphate of potass and irou is formed.   When more complicated bodies are to be formularised, brackets have often to be used.   Thus, $2\,(FeO\,SO_3,\,KO\,SO_3)$ would indicate 2 equivalents of the double salt already deseribed.

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## SECTION III.

### MODE IN WHICH CHEMICAL ACTION IS INFLUENCED BY OTHER FORCES.

THIS subject has beeu partly referred to in a preceding sectiou. It is clear that most other forces may iufluence chemical actiou in some way; for iustance, gravitation: thus, when an acid acts on a substance like peroxide of manganese, the peroxide falling in a heavy powder to the bottom of the vessel is much less likely to be speedily acted ou than if it were diffused through the liquid.   Agäin, when muriatic acid is made to act upon chalk or carbonate of lime, it disengages carbonic acid much better than the sulphurie acid does, because the latter forms the sulphate of lime, a heavy substance which surrounds the remaining chalk and elogs it, and prevents the action going ou; while the salt whieh the muriatic acid forms iu setting free the carbonic acid, viz., the muriate of lime, is perfectly soluble, aud leaves all the ehalk at the mercy,

* Many symbols perfectly represent bases, others do not without being written as proposed.   For instance, it is perfectly clear that KO is a base, but it is not so well known that $C_2H$ is one ; otherwise this  distinction in the use of the comma would be valueless.

as it were, òf the muriatic acid. In short, as a certain degree of time is requisite in chemical action, whatever interferes so as to prolong the time in which the action may take place, is so far a controlling force. There is thus hardly a force in nature which may not, more or less, be taken into consideration. But the chief of these forces are what have been just mentioned in Section I., viz., cohesion, heat, light, electricity, catalysis, fermentation, and vitality.

Cohesion obviously interferes with chemical action, and is generally an obstacle, as by binding the particles of bodies together, it tends to retain them in their homogeneous character. Hence, all the contrivances for weakening cohesion by mechanical pressure, and by solution, and the application of heat. The solid, liquid, and gaseous states of bodies are owing simply to the mode in which they are affected by heat ; and, except in a few cases, there is no substance which cannot by a great heat be converted into a liquid, and then a vapour : or by a sufficient exposure to cold, especially along with condensation, be reduced from the form of gas to that of liquid, and then to the solid form. In the gaseous form the cohesion of the particles of a body is destroyed, and the separation of the particles of gases appears in several instances to be an obstacle to chemical union. Several gases are induced to combine by condensation. Gases do, however, frequently readily combine, but, on the whole, bodies combine most readily in the liquid form. The effect of cohesion in preventing chemical action may be illustrated commercially by the higher price which native peroxide of manganese bears in the market when of a friable nature, owing to its being so much more readily acted on by acids.

Heat influences chemical action very powerfully, mostly by lessening cohesion and bringing one or more of the substances to be united to the fluid state ; but also because many bodies unite under the influence of a high temperature which will not otherwise do so. This is especially the case in combustion, where the union of two different substances is attended with the evolution of heat and light. But there are numerous instances in which heat produces decomposition : as, for instance, with several explosive compounds. But, in some cases, cold effects combination, as, for example, when oxygen gas is mixed with a certain proportion of nitrogen gas and exposed to cold, in order that the two elements may unite and form nitrous acid.

The mode in which heat operates, therefore, in bringing about chemical phenomena is not very clear, but depends upon the intimate and occult qualities of substances.

The evolution of heat itself, and especially along with light, con- stitutes, under the name of combustion, one of the most remarkable phenomena of chemistry. In general, when the union of bodies is attended with the evolution of heat, there is condensation afterwards. Thus, when sulphuric acid and water unite, there is great heat evolved, and the mixture occupies a much smaller bulk than the two separate bodies did. When gases combine to form liquids, and liquids solids, the same is mostly the case. When oxygen and hydrogen

unite to form water, there is enormous evolution of heat, and the water formed only occupies $\frac{1}{1700}$th of the bulk of its constituents. In the same way, when water and lime unite, and the water becomes solidified to form a chemical compound with the lime, much heat is produced. On the other hand there are exceptions, some real, others apparent. Thus, in the explosion of gunpowder, the gases formed occupy much more bulk than did previously the gunpowder. When many crystals are dissolved in water, great cold is often produced; and in this way freezing mixtures are formed.* But here the result is attempted to be explained by the liquefaction of the water of crystallisation contained by the salts.

The distinction between combustible and non-combustible bodies and supporters of combustion, is imaginary. There is probably no body which, if heated sufficiently, or otherwise treated, could not be placed in circumstances to make it combine with some other body, with evolution of heat and light. Oxygen gas is called a supporter of combustion, and carburetted hydrogen a combustible; but oxygen, surrounded with an atmosphere of carburetted hydrogen, would burn in it.

The doctrines of specific and latent heat have much to do with explanations of combustion. By the former term it is meant, that different bodies, at the same temperature, contain unequal quantities of heat; and this is proved by such facts as the following :—If a given volume of water at 100°† be mixed with the same volume of quicksilver at 150°, instead of the mean of 125°, which would be produced if equal bulks of water at these temperatures were mixed, the temperature will only be 120°. The mercury, therefore, has lost 30°, and

* The following are some of the best freezing mixtures, with and without ice. For readiness, 1 part of carbonate of soda, 1 of nitrate of ammonia, and 1 of water. If the materials are in proper quantity, and suitable precautions taken, the thermometer may thus be lowered between 50 and 60 degrees. The most powerful freezing mixture, without ice, that can be made, is got by mixing together 9 parts of phosphate of soda, 6 of nitrate of ammonia, and 4 of dilute nitric acid. With snow, the most powerful are obtained by mixing it with dilute muriatic or nitric acid, or with muriate of lime and potash, 3 parts of snow and 4 of potash.

† A most remarkable law has been discovered with respect to the relation subsisting between the specific heats of bodies and their atomic weights; that is to say, the specific heats of bodies give, when multiplied by the atomic weights, a constant quantity. So that if this constant quantity were divided by the specific heat, it would give the atomic weight; and it has been proposed to alter the atomic weights of some bodies which are apparent exceptions. Now, as most of the exceptions still give multiples of this quantity, and as we have seen that there is great question whether some atomic weights should be doubled or others halved, this might be done, were it not for one or two serious exceptions. For instance, arsenic and phosphorus give very different results this way, although the one is still a multiple of the other; and these bodies are so analogous otherwise, that any very great difference in their case is hardly allowable.

the water only gained 20°, so that the same quantity of heat has a greater effect in heating mercury than in heating water. Hence it is inferred, that the capacity of water for heat is to mercury as 3 to 2 : but as this only refers to equal volumes, and mercury is $13\frac{1}{2}$ times heavier than water, the latter will have a capacity to the former, if we take equal weights, of $\frac{2}{3} \times 13\frac{1}{2}$, or $20\frac{1}{4}$. Owing to this cause, the mercury is always heated and cooled much sooner than water, because it takes less heat to raise it to a given point, owing to its capacity, or specific heat being less, and shorter time to cool it down.

Now it has been supposed, that when chemical union is attended with diminution of specific heat in the compound formed, this might account for the evolution of heat.

Again, the latent heat of bodies bears the same relation to different *forms of the same body* that specific heat does to different bodies ; for it can be proved, that at the same temperature the different forms of the same body contain very different quantities of heat. Thus, when a piece of ice is brought into a warm room, it begins to melt ; but until it is all melted, it continues at the temperature of 32°. During all this time, it receives heat which is not measured by the thermometer ; this heat is therefore lost—or it is expended in changing the *form* of the ice. Or if ice, in melting, be placed in the same circumstances as water, it will be found how soon the temperature of the water rises, when heated, in comparison with the ice, until the latter is melted, when it rises equally with the water. In the same way, when liquids become gases, or vapours, a great amount of heat is expended in changing the form.

Now, these facts are reversed when liquids become solids, or gases liquids—the latent heat is then given out.

It was natural, therefore, to apply these facts to the explanation of chemical changes, accompanied with changes of form and of density, where there is evolution of heat or production of cold ; but, for reasons partly already assigned, the matter cannot thus be altogether explained.

Combustion is not only one of the most striking phenomena of inorganic chemistry, but it plays an important part in the organic life of animals and vegetables ; the processes of respiration and support of animal heat being now known to be a true combustion, capable of explanation on similar principles with combustion itself.

The dependence of combustion on chemical action may be illustrated by such an instance as the following :— When potassium, which has a strong affinity for oxygen, is put into a jar of oxygen, it will not burn spontaneously ; but when thrown upon water or ice, it instantly takes fire. Here it has a double affinity for the constituents of the water, combining at once both with the oxygen and the hydrogen ; hence the combustion.

The effect of light in producing chemical changes is shown principally in its power of enabling chlorine, in solution in water, to decompose it ; and still more so in the beautiful processes and arts which have been discovered by Talbot and Daguerre. The chloride

of silver and other metallic salts are decomposed in these processes, and their various oxides precipitated. These effects are produced more readily by the violet rays of the solar spectrum than by the others; but as the effect can be produced more readily if the exposed substance to be decomposed is carried out of the spectrum altogether on the violet side, the rays which produce the effect are not the same as the other rays, and are called chemical rays. It is probable that these chemical rays may exercise a very considerable influence on the chemical phenomena of vegetable life.

Electricity powerfully affects chemical action. The ordinary electric spark, passed through many gaseous mixtures, causes them to unite, as, for instance, oxygen and hydrogen; but it is in the form of voltaic electricity that this power is most remarkably exemplified. In fact, the whole theory of chemical action is now connected, both in principles and terminology, with the theory of electricity.

In proceeding to explain this, it will be necessary for the reader to bear in mind the nature of electrical induction or polarity.

This is a subject with which young students of chemistry experience no ordinary difficulty. It may be well here to discard all unnecessary refinement, and to give as clear an idea as possible of what may be often deemed the essence of one of the most difficult matters in chemistry.

When once electricity is excited in a substance, it is due to a disturbance of the electric balance or equilibrium previously maintained. In ordinary frictional electricity, as produced by the common electric machine, the substance which, on being rubbed with another, developed electricity, was supposed to have absorbed electricity from the latter, and to have become *positive* while the other was supposed to have lost electricity, and to have become *negative*. Instead of this view another theory was started, viz., that by the various means employed different states or kinds of electricity were developed. After the discovery of chemical electricity, or galvanism, the terms positive and negative were applied principally to the different states in which the opposite poles of the galvanic battery were found to be; but the clearest idea of the matter appears to be derived from the phenomena of magnetism, which we now know to be identical with electricity, and the word polarity seems to convey the best idea of what occurs when the electric equilibrium is disturbed.

When the magnetic state is excited in a metal, it is well known that the two extremities of the magnet have opposite properties. These properties are supposed to have neutralised each other before the electric or magnetic equilibrium was disturbed in the bar in which they resided, and then to have become separated, and gone to the two extremities, and thus to be able to manifest their properties.



Diagram No. 2.

The shaded parts will represent one of the boreal poles, the unshaded the austral; in the centre of the bar no magnetism will be perceptible, because the two forces will hold each other in check; but if the bar were cut asunder new poles would appear at the extre-

mities of each division ; but it must be remembered, that there is one thing which such a diagram cannot show, viz.,—that according to the number of the chequered spaces will be the intensity of the magnetic force which every pair will develop, every white space being supposed from one extremity to the other to increase the different and opposing force next it, represented by a black space, the latter space to increase that of the white ; and this kind of influence will be reciprocally transmitted back from the other extremity of the bar, so that at one side comes to be manifested the whole of the one force, and at the other the opposite force.

In the simple voltaic circle, as it is termed, where two metals, as zinc and copper, are used, the same kind of polarisation may be supposed to take place.*   Wherever two metals of different chemical affinities are placed in contact with a fluid for the elements of which their affinities differ, it may be supposed that the electric equilibrium is destroyed through their polar influence.   In the accompanying simple



Diagram No. 2
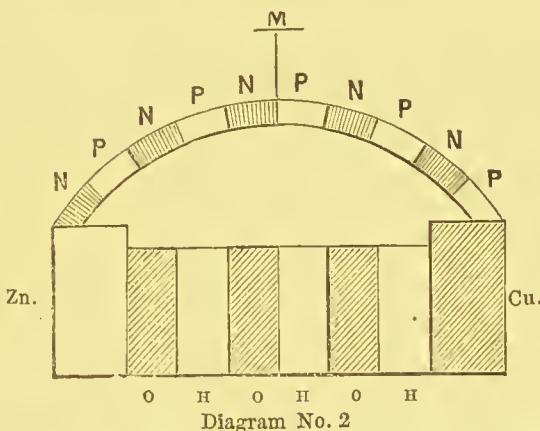
diagram there are two plates of zinc and copper, with a connecting medium, in contact with water ; for although with this fluid there is but little action, yet the principle is the same as if an acid liquid, where there is much action, were used.   In this diagram the zinc is supposed to be in one electrical state, and the copper in another, and through them the intermediate water to be polarised, the electric or chemical equilibrium between its particles destroyed, so that they exert their mutual affinities ; the particle of oxygen next the zinc having an affinity for that metal, will combine with it ; but this will set free an atom of hydrogen ; that being in the nascent state, or just coming into existence, in which state the chemical power of all bodies is greatest, will decompose the next atom of water and take its oxygen, setting free another atom of hydrogen, so that at last, this action going on

* Zinc and copper are taken as examples because of their common use, and because, for a long time, they were the two chiefly used in galvanic apparatus; but any others, of different chemical affinities, would do as well.

through the fluid, there will remain a particle of hydrogen next the copper which will escape, not having an affinity for it. The poles were called positive and negative from the supposed direction of the electrical current; but, retaining the terms positive and negative, it is preferred here to explain the theory of the voltaic circle entirely upon the hypothesis of polarisation. Here the zinc plate is positive and the copper negative. But supposing the connecting medium from the positive zinc to the negative copper completing the circle to be polarised, as the water was in the chemical action, then what will take place, or may be supposed to take place, will be illustrated in the diagram on the same principle as in the magnet; and if the connecting medium completes the circle from Zn to Cu, no poles will exist, the electric equilibrium will remain undisturbed or be restored, which is precisely what takes place when a wire of sufficient capacity passes from one end to the other of a galvanic battery; but let this wire be severed at M, and there will be two magnetic or electrical poles, the one from the copper, positive, the other from the zinc, negative, with all the accumulated tension of the series of vibrations which have taken place in the battery or magnet.

The explanation of what takes place in a compound voltaic circle is similar. Let diagram No. 3 represent a compound voltaic
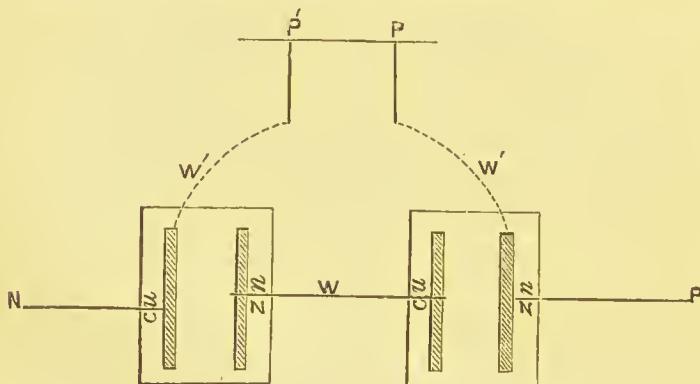


Diagram No. 3.

circle. Here the junction of the copper and zinc by the wire W, the conducting medium, has for its effect to increase the length of the polarising medium, it is in short increasing the number of vibrations, or whatever they are, by which the intensity of the electric force is augmented, until at length, as in the former diagram of a simple voltaic battery composed of a single pair of plates, all the positive electricity is in the zinc, and all the negative in the copper, as in the former case. But, supposing the circle to be continued by W,' W' from the copper and zinc poles, if these meet the circle will be completed, and the equilibrium be restored. If interrupted as in the diagram at P, P', and these become poles, then, precisely as was shewn in the second diagram, the extremity of the conductor from the copper will

be positive, and that from the zinc negative; and, if these poles be placed in water, the battery being of sufficient intensity, *i. e.* consisting of a sufficient number of pairs of plates, and these of sufficient power, or the battery sufficiently charged, the oxygen will appear at P', and the hydrogen at P ; or, if such a battery were employed to decompose potassa, the electro-positive metal potassium would appear at P, and the oxygen at P'.

Thus it is easy from these considerations to deduce such inferences as :—1. That a most close connexion exists between electricity and chemical affinity; the only difficulty being, in such cases of galvanic action, to determine whether the chemical action produces the electricity, or the electrical polarity precedes the chemical action. 2. That these being, at all events, closely connected, the power of a galvanic battery will depend upon the relation of the solid or metallic elements to themselves and the fluids used to charge the battery; the more diverse the former in their electrical and chemical nature, the greater will be their polarising power ; and the greater the chemical energy of the fluid elements, the greater will be the reciprocal action between them and the solids.

As it is seen in the phenomena of ordinary electricity, and especially of magnetism, that substances in opposite electric states attract each other, and in similar electric states repel each other, so it is supposed that, in chemical action, the attractions of substances for each other may be accounted for by their tendency, when brought into contact, to assume different electric conditions. Thus, when oxygen and hydrogen are separated by the decomposing action of galvanism, the latter, as we have seen, will appear at the wire connected with the zinc, the former at that connected with the copper ; and as the extremity of the wire from the zinc is electro-negative (although the zinc itself is electro-positive), the electro-positive hydrogen is attracted by it ; and, in like manner, the extremity of the conductor from the copper being electro-positive, although the copper itself is electro-negative, the electro-negative oxygen makes its appearance there. Whenever, therefore, a substance is decomposed by galvanic action, that one of its elements which appears at the wire connected with the last zinc plate is electro-positive ; that which appears at the wire in connection with the last copper is electro-negative. This explanation, it is hoped, will save much confusion.

All substances, then, upon the electro-chemical theory, are divided into electro-negative and electro-positive. The electro-negative substances are chiefly oxygen, chlorine, bromine, iodine, and those bodies which energetically produce chemical phenomena. But it must be remembered that no substance is absolutely electro-negative or electro-positive. The relationship is entirely comparative. The general rule is, that the element or compound is more electro-negative than another which it can dispossess from its combination with an electro-positive base ; thus chlorine will dispossess bromine, and the latter iodine from combination with potassa.

The more electro-positive bodies are some of the metals. Probably

potassium may be selected as one of the best examples; but some of the metals are electro-negative, as arsenic, antimony, &c.

Now, when two electro-negative bodies combine, one, of course, of them being less electro-negative than the other, but relatively electro-negative to other bodies, the result is a compound itself electro-negative. Such are the compounds of oxygen with chlorine, bromine, and iodine; with phosphorus, sulphur, &c.; these bodies are called *acids*, and are characterised by their sharp, sour taste, by their reddening vegetable blues, and by the avidity they show for combining with the opposite class of compounds, the *alkalies*. When an electro-negative body combines with an exactly electro-positive body, which, perhaps, hydrogen may be, the result is a neutral body, which water appears to be, since it combines equally with acids and alkalies. When, on the other hand, the combination is with a powerfully electro-positive body, such as potassium, the result is an electro-positive substance, an alkali, which colours vegetable blues green, neutralises acids, and has an acrid taste, altogether different from that of the acids. In another *class* of compound substances the electro-positive character is less strongly marked, but sufficiently so to enable them to form very stable compounds with acids; such are the earths and oxides of metals; but many metals form acids with oxygen, such as arsenic, antimony, titanium, &c.

If the electro-chemical theory could be carried out, diagrams might be framed upon it, so that, if the electrical position of every element could be assigned, their probable action and the nature of the compounds they could form might be deduced. In the present state of our knowledge this cannot be done.

It should be remembered that the precise views entertained with regard to the electrical nature of the chemical action between the elementary bodies, are held with regard to all combinations; thus, when the chloride of mercury (corrosive sublimate), combines with the chloride of potassium to form a double salt, the mercurial salt is considered to be the acid, and the chloride of potassium the alkali.

The power or force termed catalysis has a very singular action on chemical phenomena. If a piece of spongy platinum or iron in fine powder be put into a mixture of oxygen and hydrogen gases, it causes them to unite and form water. At one time it was thought that the absorption of the gases into the pores of the spongy platinum, and their condensation by a species of capillary attraction, explained the fact; but it has since been ascertained that the plain metal possesses the same power; and numerous facts of the same character, *i. e.*, showing the power of some bodies to produce chemical changes from a mode of operation at present little understood, have been brought under the same head; for instance, many metals, and even metallic oxides, cause the decomposition of peroxide of hydrogen with explosive violence, without themselves undergoing any change. Perhaps the explosion of the quadrochloride of azote by simply touching it with a rod oiled at the extremity, may be a fact of the same kind. Phenomena of this kind have been referred to an occult influence, and grouped together, and the force has been called catalysis, simply because there seems no other

mode of accounting for what takes place, and thus these phenomena are categorised under this title, until science is able to explain their nature.

Fermentation is a species of catalysis. When diastase, the principle which exists in yeast, is brought in contact with starch or sugar, it causes their resolution into carbonic acid and alcohol; but the diastase itself undergoes no change; nor can what takes place be explained on any known law.

Vitality, in like manner, can produce changes inexplicable by any ordinary chemical laws. Substances are formed in living vegetable and animal organisations, and processes carried out which cannot be conducted in the laboratory. Just as in the photographic and other processes of the kind, effects are produced by means of the rays of light which we cannot exactly accomplish in any other way; but the *results* in these cases are not the less *chemical*. So is it in the living body; the *facts of life* are not the less physical and chemical because accomplished by other than the ordinary physical and chemical forces. The circulation of the blood is a physical fact, although it is not a physical force which sets the heart in motion. The production of the various chemical compounds which exist in the urine from the blood and secretions, are all chemical facts, although we may not be able to understand how these compounds are formed.

All attempts to check the application of chemistry, therefore, to the explanation of the chemical processes which take place during life on the ground of their vital character fall to the ground, just as much as if we were prepared to deny that in the photographic process oxide of silver was not reduced and chlorine set free, *because* this was done by the influence of the rays of light.

## ISOMORPHISM.

Many beautiful relations of form exist among elements and compounds possessed of analogous properties.

It has been supposed that the crystalline forms of compound bodies bear a definite relation to that of their elements. But the crystalline forms of many elements are unknown; and others, such as sulphur, crystallise under two forms, or are said to be dimorphous. The term isomorphous is applied to bodies which can replace each other in combination without producing any essential difference in the crystalline form of the compound. For instance, in the various alums, such as the common alum and iron alum, the sulphate of iron and sulphate of alumina can replace each other in combination with sulphate of potass, without any difference in the form of the crystals. Some of these substances which replace each other in this way are not even themselves similar in form, as, for instance, titanium and tin; sometimes the constituents replace each other by an equal number of atoms— sometimes by an unequal number.

Although in general similarity of form does connect itself with similarity or analogy in other respects, this is not always the case.

The general chemical analogies of isomorphous groups are remarkably characteristic. No class of bodies is more closely related

than the class of chlorine, bromine, and iodine. Thus the chemical equivalent of chlorine is the lowest, that of bromine next, then that of iodine; chlorine is a light green gas, bromine a red fluid, and iodine a violet solid. All the compounds in their physical and chemical relations obey the same beautiful and symmetrical analogies. They do so also in their physiological and medicinal properties; and chlorides, compounds of chlorine with metals, are isomorphous with bromides, and these with iodides. The compounds formed by the acids of chlorine and its allied bodies with oxygen united to a base, chlorates, bromates, and iodates, are all isomorphous. In the same way barium and lead are isomorphous, and their general chemical properties are remarkably alike; but, there are other instances of isomorphous groups where the general chemical analogies are not so strong.

### ALLOTROPY AND ISOMERISM.

By allotropy is meant the fact that a body may exist in two or three different forms without any recognisable chemical change. Cinnabar may exist either as a black solid or as the fine pigment vermillion. But one of the most singular instances of the kind is afforded by the iodide of mercury, which when sublimed is of a beautiful yellow colour, but when struck a sudden blow becomes of a splendid red.

By isomerism, is expressed the fact that there are substances of the same chemical constitution as far as analyses go, which, nevertheless, exist in different forms, not merely as regards colour and such like properties, but chemically distinct. For instance, there is the compound of carbon and azote, the bicarburet of azote, which in the form of cyanogen is a gas, and in the form of paracyanogen a deep black solid, and differing in other respects; each of these bodies contains two atoms of carbon and one of azote, and it has been supposed that the atoms might be differently arranged, so that the one body should be written C N C, and the other N C C. If these views were correct there might be nearly as many compounds of a body as its atoms were capable of being transposed, according to the law of combination and transformation in algebra.

### DOCTRINE OF SUBSTITUTION.

As in isomorphism one substance may be substituted for another in a crystalline compound without change of form, so one element of a compound of similar chemical properties may be substituted for another, and a new compound formed. In organic chemistry there is a class of bodies: viz. formic acid, chloroform, bromoform and iodoform, where this may be well observed. Each of these bodies contains a radical-formyl, whose symbol is $C_2H$. Now, if three atoms of oxygen are added to the two of carbon and one of hydrogen, we get $C_2HO_3$, or formic acid; if three of chlorine be substituted by a suitable chemical process, then $C_2HCl_3$, or chloroform is obtained; if three of bromine, then $C_2HBr_3$; and if three of iodine, then $C_2HI_3$; and all these bodies are possessed of analogous properties—physical, chemical,

and physiological. Here the strict association in electro-chemical properties between these elements would render the substitution probable, so that it may be laid down as a law that when one substance is combined with a base, another chemically similar may replace it, and if the substance be crystalline, probably without alteration of the crystalline form.

## CONSTITUTION OF SALTS.

The names of some compound bodies are so written as to express a particular view with regard to the mode in which the elements exist in them. When there is only one equivalent of each of its constituents in a binary compound, there can only be one way of writing the name. Thus, we can only say $NO$ in writing the symbol for the protoxide of azote; but when we have $NO_5$, or nitric acid, particular views may be entertained as to the way in which the five equivalents of oxygen are combined with the azote, whether all directly, or with the element, or whether some intermediate compound is first formed. There are particular facts which might lead to the conclusion that in this case the first compound formed is $NO_2$, and that with that body more oxygen is afterwards combined: one reason is, that in decompositions of nitric acid, this compound, the binoxide of azote, is so often formed, as if there were a strong tendency for the one equivalent of azote to unite with two of oxygen; and the facility with which the binoxide of azote takes oxygen from the air is another reason.

Again, in the case of the peroxide of hydrogen, we cannot, looking at the facility with which the body gives off oxygen and becomes water, but conclude that the excess of oxygen is combined with the water. Thus, $HO,O$ would be the correct mode of writing the symbol of the peroxide, and not $HO_2$.

Again, peroxide of potassium, when put into water, speedily loses its excess of two equivalents of oxygen, and a solution of water is formed. The symbol here, therefore, would be $KO,O_2$, and not $KO_3$.

In organic chemistry, this mode of looking at the basilar constitution of compounds, frequently throws considerable light on their nature, and is sometimes a guide to the discovery of new bodies, by teaching us when, by the doctrine of substitution, one substance can be connected with a base instead of another. Thus, in alcohol, there is supposed to be a compound radical called ethyl, whose formula is $C_4H_5$; ether is the oxide of this, $C_4H_5O$, and alcohol the hydrate of the oxide, $C_4H_5O,HO$; and the substitution of the respective elements for $O$ in the oxide, produces the chloride $C_4H_5,Cl$, the bromide $CH_5,B$, the iodide $C_4H_5,I$.

Like the elements compound radicals may be divided into two great classes, the *basyl* class and the *salogen* class; the former are the compound electro-positive bases, such as potassa, the latter the electro-negative acids.

*Salts.*—Two different views may be entertained of the nature of salts. At one time every acid was supposed to contain oxygen, and salts were regarded as compounds of an oxide with an oxacid. Thus

the muriate of soda was considered a compound of muriatic acid, and an alkali the oxide of sodium, at the period when Davy discovered the compound nature of soda. Muriatic acid was supposed to be a compound of *murion* and oxygen, with one equivalent of water. In oxymuriatic acid, or chlorine, it was supposed that one equivalent of oxygen took the place of the equivalent of water. So that the holders of this view did not differ from chemists of the present day with regard to the equivalents of these bodies. In round numbers, they made chlorine 28 real muriatic acid and 8 oxygen = 36, and ordinary muriatic acid, 28 real acid and 9 water = 37. Davy proposed to call chloride of sodium a binary compound; and he altered all the views entertained of the constitution of salts of hydracids on the same model. The discovery of bromine and iodine gained the assent of chemists to Davy's views; and now many explain the constitution of all salts on the same model, by creating a new class of salifying compound radicals.

For instance, the ordinary mode of writing sulphate of soda is $NaO,SO_3$; but many now would write it $NaSO_4$, making a direct compound between the metal sodium and a new compound radical, *sulphion*, as it is termed. In the same way hydrated sulphuric acid, a compound of 1 eq. of acid and 1 of water, sulphate of water, $HO,SO_3$, is made *sulphionide* of hydrogen $H,SO_4$; so all the salts of sulphuric acid can be similarly written. In the same way salts of nitric acid are turned into nitrationides, and so forth. Advantages are claimed for this mode of viewing the constitution of salts: but the best division seems that of Professor Graham, who divides salts into—

1. Those which have an isolable salt radical,— simple or compound— as the chlorides, bromides, iodides, sulphurets, cyanides, &c.

2. Those which contain an isolable acid,—sulphates, carbonates, &c.

3. Those which neither contain an isolable acid nor an isolable salt radical,—nitrates, hyposulphites, &c.

There are also three classes of oxygen salts :—

1. Monobasic salts, in which one equivalent of acid is combined with one of base; thus the sulphates are mostly of this class. These salts combine with several equivalents of water, and often crystallise under different forms, according to the number of equivalents of water which they contain.

2. Bibasic salts, where two equivalents of base are united with one of acid.

3. Tribasic salts.

Subsalts are supposed to be formed by the substitution of an equivalent of base for an equivalent of water of crystallisation in a salt; so that the base comes to be greatly in excess.

Double salts are formed to a great extent; and the doctrine of substitution applies to the formation of many of the class.

### AMMONIUM DOCTRINE.

This theory is somewhat similar to the sulphion theory, in creating an imaginary new radical.

Ammonia is a gas composed of one eq. azote and three of hydrogen. It dissolves in water, and forms a strong caustic alkaline solution which neutralises acids like potash and soda. But all its oxygen salts contain one eq. of water, without which they cannot exist : they are isomorphous with the salts of potash. Hydrochloric acid unites directly with ammonia without losing its hydrogen, forming, therefore, a hydrochlorate or muriate, and not a chloride. Now it is supposed that ammonia, with the addition of another atom of hydrogen, becomes $NH_4$ a metal, to which the name of ammonium has been given; and thus muriate of ammonia would be $NH_4,Cl$ instead of $NH_3,ClH$. Sulphate of ammonia $NH_3,HO,SO_3$, would become $NH_4,O,SO_3$, a sulphate of oxide of ammonium, or $NH_4,SO_4$.

The metal ammonium is not so entirely imaginary as the existence of sulphion. When mercury alloyed with one per cent. of sodium is poured into a saturated cold solution of sal-ammoniac (muriate of ammonia), it swells enormously, becoming about 200 times larger, acquires a consistence like butter, and retains its metallic lustre; at the same time it gains not more than ½000th in weight. Hence it is supposed that the sodium of the amalgam sets free ammonium by combining with its chlorine, leaving the mercury to combine with the ammonium, and that the singular substance formed is a genuine amalgam.

# PART II.

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## ELEMENTARY NON-METALLIC BODIES.

SOME have proposed to call elements metals. To do so is simply to throw away a useful word. It is true that the metallic characters of elementary bodies are sometimes difficult of definition, so that there may be nearly as much reason for styling bromine a metal as for applying that term to mercury, especially as electro-negative metals are admitted. But it is true, what we invariably find in nature, one class gradually slides into another, the distinctions which indicate the transition being too subtile for our definition; it is, as Lord Bacon said, the subtilty of nature is too great for the subtilty of art. But yet we know very well that oxygen should not be classed under the same head as gold.

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## 1. OXYGEN, O.

Equivalent 8 ; combining measure ☐ half a volume; sp. gr. 1,105·6 (to air as 1,000).

This substance is the most extensively diffused of all bodies, forming about a fifth of the air, $\frac{8}{9}$ths of the ocean, and in the form of oxides, acids, and salts, a large portion of the crust of the earth. The ordinary processes for obtaining oxygen admit of being classified as follows :—

1. Those in which the gas is obtained from a metallic oxide by means of heat.

2. From a metallic oxide by the aid of heat, assisted by the affinity of an acid.

3. By the action of heat on a salt of a highly oxygenised acid.

The decomposition of the black oxide of manganese, of red-oxide of mercury, and of red lead, are examples of the first-class.

Black oxide of manganese is a compound of the metal manganese and oxygen in the proportion of one equivalent of the former, or 27·67, with 2 eq., or 16 of the latter. Three of these equivalents of this peroxide or binoxide lose 2 eq. of oxygen, $i.$ $e.$, 130·01 of the material will give 16 of oxygen. What takes place is this—
$$3 \ MnO_2 = Mn_3O_4 + 2 \ O.$$

The peroxide should be heated in an iron bottle; the quantity to be used should depend upon the amount of gas required; a pound of good manganese should yield about 5 gallons or more. When oxygen gas is collected in this way, it should always be tested before being used. This is easily done by collecting it and putting a match just blown out into it, when, if the oxygen be pure, the match will be rekindled.

The annexed drawing (No. 4), shows the apparatus or gas holder used for storing up gases; when the reservoir B is filled from the cistern A through the tube $c$, the stopcock in $c$ is turned, and the mouth of a gun barrel coming from the iron bottle containing the per-oxide, and which is heated in a furnace, is inserted. The gas as it comes off rises in B, displaces the water which flows out at $f$ until the level of the water falls to $f$; $f$ is then closed, and the vessel remains full of gas. The orifice at $f$ is then closed by a plug. When gas is wanted the cistern A is kept filled with water as the gas is expelled. The gas escapes either into the well by means of $d$, when a jar can be filled, or at the stopcock $h$, where



Fig. 4.

a flexible tube can be attached. $e$ is a glass tube inserted into the gas holder, which enables the amount of the gas in B to be measured.

Oxygen may also be prepared by heating the red oxide of mercury in a green glass retort. Here the whole of the oxygen is given out, and the oxide is resolved into mercury and oxygen, but on account of the large equivalent of mercury, this process yields very little gas, and is expensive. The red lead only loses part of its oxygen.

When sulphuric acid is heated with the peroxide of manganese, a sulphate of the protoxide is formed, and 1 eq. of the peroxide loses one of oxygen. Thus, $MnO_2 + SO_3 = MnOSO_3 + O$.

But the most abundant source of pure oxygen is obtained from heating the chlorate of potass in a flask. This salt is a compound of chloric acid and potassa. The chloric acid is composed of 1 eq. chlorine, and 5 of oxygen; the potassa of 1 eq. potassium, and 1 of oxygen. Now, when heat is applied to this salt it first melts, and then is decomposed at nearly a red heat, and then gives off all its oxygen, leaving nothing but chlorine and potassium in combination in the vessel in which the decomposition has taken place. Thus in the formula $KO,ClO_5 = KCl + 6O$, we see what has taken place: 1 eq. chloride of potassium remains, and 6 of oxygen have been evolved. The best apparatus for conducting this process is a flask of green glass with a bent glass tube inserted in it by means of a cork. The gas can be collected in a gas holder, as in fig. 4, or over a pneumatic trough. Fig. 5 represents this latter mode of



Fig. 5.

collecting a gas over water. $a$ is the delivering tube, $b$ the gas over the trough. This process is much facilitated by mixing the
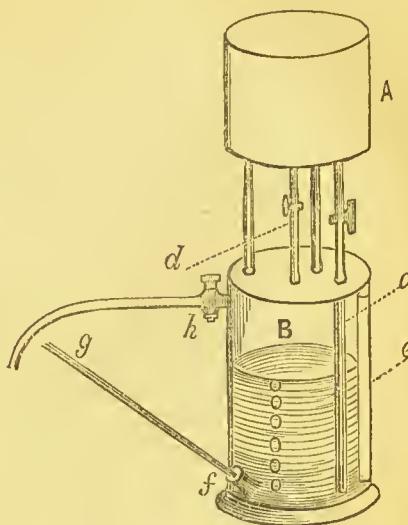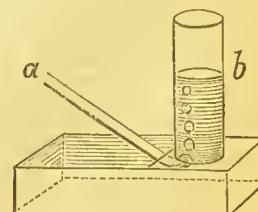
chlorate of potass with peroxide of manganese. One-twelfth of the peroxide answers very well, but more may be added. Other processes have been recommended for preparing oxygen, but the above seem enough for practical purposes.

Oxygen gas has neither smell nor taste, and is colourless; 100 cubic inches of it, at the temperature of 60°, and barometer at 30 inches, weigh 34·19 grains. It has not yet been reduced to the liquid form.* By great pains 100 cubic inches of boiled water, with its air thus expelled, may be made to absorb 3·5 of oxygen: it is therefore very sparingly soluble in water.

Oxygen is the great supporter of combustion, which arises from the extent of its affinities and its ubiquity. It has already been explained, that this term, supporter of combustion, is merely relative, and that bodies would support the combustion if the oxygen were introduced into them, as oxygen supports their combustion when they are introduced into it.

The following examples may be cited as appropriate experimental illustrations of combustion :—

1st. As illustrations of the nature of combustion : A piece of potassium, which does not fire spontaneously in the air, or even in oxygen, may be thrown into water, or on ice. A brilliant combustion will take place, owing to the decomposition of the water, and its resolution into potassa and hydrogen, which latter also is said to form a compound with potassium, and again to undergo combustion. This experiment may be taken to show the relationship between combustion and chemical affinity. Then a quantity of chlorate of potass, in coarse powder, may be put into a precipitate jar, as in fig. 6, and water poured upon it. Then a few pieces of phosphorus being thrown in, a little sulphuric acid may be introduced through the tube funnel shewn in the drawing. Almost instant action takes place, a green coloured gas is disengaged, and the phosphorus takes fire under the water. This is due to the evolution of a highly oxygenated compound of chlorine and oxygen, which is decomposed by the phosphorus, and the result is combustion, quite independent of the presence of the water.



Fig. 6.

2nd. As illustrations of the formation of acids by oxygen : A little charcoal, sulphur, or phosphorus, may be put into the spoon, (fig. 7), known as a deflagrating spoon, inflamed, and introduced into a jar of oxygen gas—they will burn brilliantly. The carbon, or charcoal, will form a gas which, if a little water be introduced into the jar and shaken in it, will be absorbed, and be found to colour blue litmus slightly red, and to give a precipitate with lime-water—the carbonate of lime : carbonic acid then has been formed. The sulphur will burn with a splendid blue flame, and form acrid fumes, which, on being



Fig. 7.

* The mode in which gases are reduced to the liquid form under the pressure of their own vapour will be explained under *Air*.

absorbed by water, will redden and then bleach vegetable blues—sulphurous acid; and the phosphorus will form abundant white acid fumes, which will settle in a white powder, containing more than one acid compound of phosphorus and oxygen.

3rd. A little potassium may be put into a clean spoon, set fire to, and burnt in oxygen. It will burn very brilliantly. The spoon should then be allowed to cool, and put into a little water. An escape of gas will take place—the evolution of excess of oxygen, for a peroxide of potassium has been formed, and the water will have become of an excessively acrid alkaline taste, to render turmeric red, and turn infusion of cabbage-green—an alkali potassa, has been formed.

4th. A piece of thin iron wire is to be twisted into a spiral form, and a little sulphur to be melted at one extremity of it, so as to adhere, while the other end is to be connected with a broad cork. The sulphur is to be inflamed, and the wire introduced into the gas. It will burn with brilliant sparks, and an oxide is formed.

5th. The combustion of oxygen with hydrogen forms an instance of a compound of oxygen, differing in some respects from all these classes, inasmuch as it can combine alike with acids and alkalies.

Bodies evolve heat in proportion to the amount of oxygen which they absorb in combustion, or nearly so. This amount of heat can be measured by the time in which a certain quantity of water is raised to a given temperature by the burning body.

Independent of the sudden evolution of heat in rapid combustion, there are many processes of slow oxidation, attended with more or less evolution of heat.

The rusting and tarnishing of many metals is owing to their slow oxidation. A beautiful instance of speedy tarnishing is presented by a globule of potassium, when freshly cut in the air. At first it is brilliant as the brightest silver, but almost immediately it becomes like dull lead.

In the fermentation of alcoholic fluids, where oxygen is absorbed and vinegar formed, heat is given out, and in many animal and vegetable processes. The most remarkable instance in organic nature is in respiration, by which animal heat is maintained.

This process we now know to be a true combustion. The amount of oxygen absorbed from the air is truly enormous. A man has been calculated to absorb from the atmosphere in a year about 800 pounds weight of oxygen; and this is all employed, not directly in nourishing the body, but, like the fuel of a steam-engine, in supporting animal heat. To make the analogy between respiration and combustion greater, as ordinary combustion out of the body is principally maintained by the combustion of carbon, or charcoal, in its various forms, either alone, as in charcoal, coal, coke, &c. or combined with hydrogen, chiefly as in wood, and especially in oils and fatty substances, coalgas, alcohol, &c., so in respiration, it is articles of food, or principles analogous to these substances—compounds of carbon and hydrogen—which are burnt off by the oxygen.

Flame, as it is observed in the combustion of a candle, takes its

form in this manner:—It is the rapid combustion of volatile matter drawn up by the capillary attraction of the wick. The tallow is melted and drawn to the top of the wick; here it is boiled and converted into vapour, which ascends in a columnar form, the outer part is rapidly burned and acquires a white heat which still more volatilises an inner column which cannot get oxygen, but on ascending a little further this inner column will be burnt on the outer side—at the circumference, and will present, like its predecessor, an outer circle in combustion, and an inner one of volatile combustible matter, which itself will soon meet with a fresh supply of oxygen and repeat the same phenomenon until the flame is reduced to a point; fig. 8 will help to explain this. The most obvious point therefore in all remedies for imperfect combustion, where soot escapes, is to supply the volatilisable and volatilised combustible matter, which if it escaped would in most cases present the form of soot, with a sufficient supply of air. A is the first column, and $a$ the matter in combustion. B and $b$ represent the same in the second, and C $c$ in the third.
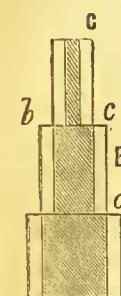
Fig. 8.

The principal chemical use made of oxygen is by employing it in the blowpipe instead of a supply of common air. This may be easily done by appending to the flexible tube attached to such a reservoir as is represented in fig. 4, a blowpipe, and through it directing a stream of oxygen on a substance whose combustion it is desirable should be accelerated. The most powerful effects may be produced by means of a combustion of the kind; or a stream of hydrogen, or carburetted hydrogen—coal gas, may be conducted so as to unite with the stream of oxygen, and be caused to unite and burn with it. In this way the most powerful heat that can be produced is attained. In the combustion thus produced, platinum, which resists the strongest heat of a smith's forge, may be melted almost like wax in the flame of a candle.

## 2. HYDROGEN, H.

Eq. 1; sp. gr. 69·26; combining measure, a whole volume $\square$.

Hydrogen gas may be obtained by the de-oxidation of water, its principal compound with oxygen, either by directly removing the oxygen by some element which has a greater affinity for the latter, or by effecting this by the indirect action of an acid. Thus, hydrogen may be obtained by passing steam over iron filings heated red hot in an iron tube or gun barrel passed through a furnace, and then connecting a tube with the iron tube or gun barrel, which passes into a pneumatic trough where the gas may be collected over water in the usual way. The oxide of iron is formed by the union of the oxygen with the iron, and the hydrogen of the water is separated. See fig. 9.

Or, as is most usual, some metal and acid may be employed, which, by the tendency of the metal to unite in the form of oxide with the

acid, causes the decomposition of the water; *i. e.*, as the metal has an inclination to unite with the acid in the form of oxide to produce a salt, and as this can only be accomplished by the decomposition of the water, so water is decomposed in order that this may take place.

Zinc or iron (especially the former) are generally employed. The zinc in the granulated form effected by fusing a quantity of the metal
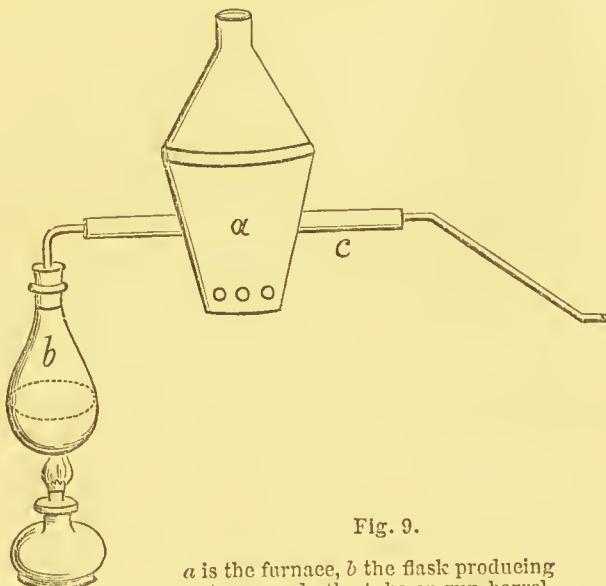


Fig. 9.

*a* is the furnace, *b* the flask producing
steam, and *c* the tube or gun-barrel.

and pouring it while in the state of fusion into cold water; the iron in the form of turnings or filings, in which state it is easily procured from various manufactories. An apparatus of the form shewn in fig. 10. is generally employed. Zinc and the proper amount of water are first put in; then the cork is secured; and then sulphuric acid is gradually introduced. The sulphuric acid having a tendency to form a sulphate with the oxide of zinc, the water for this purpose is decomposed, as the oxygen goes to the zinc, an oxide of zinc is formed with which the sulphuric acid immediately combines, forming sulphate of zinc, and the hydrogen of the decomposed



Fig. 10.

water escapes. Thus, if we have in presence $Zn + HO + SO_3$, the result will be $ZnO, SO_3 + H$ disengaged.

The proportions for the strict decomposition are 1 eq. Zinc=
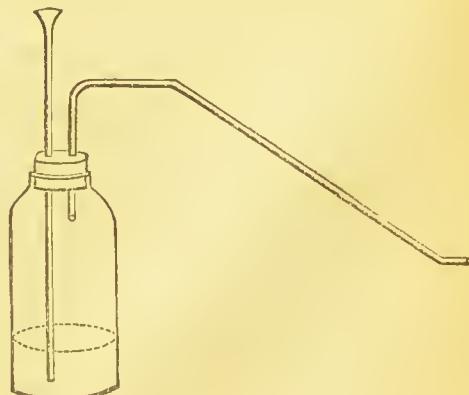
32·52, 1 eq. $SO_3$=40, and 1 eq. water=9; but the strong sulphuric acid of commerce contains 1 eq. water, and therefore the proportions required by theory should be 32.52 of zinc to 49 of sulphuric acid by weight. But it is found that a larger quantity of water accelerates the decomposition, probably by increasing the solubility of the sulphate of zinc formed, and enabling the remaining metal to be more readily acted upon. As zinc and sulphuric acid are exceedingly cheap, the best proportions in practice appear to be about three of zinc, five of sulphuric acid, and twenty-five of water by weight; but more water does not interfere with the process.*

Hydrogen gas thus obtained is colourless, the lightest substance in nature, and highly inflammable. It is often selected in practice as an example of a body itself combustible, but not a supporter of combustion. If a jar of hydrogen be lifted from the pneumatic trough and a taper applied to the orifice, the gas readily burns; but if the taper be introduced into the interior of the jar it is extinguished.

Hydrogen has a peculiar odour when prepared by most processes, which is probably owing to some peculiar and hardly known compounds generated with it. One hundred cubic inches of it weigh 2·14 grains. On account of this property of lightness it has been used to fill balloons.

Fig. 11.

When two volumes, by measure, of hydrogen are mixed with one of oxygen, or rather one volume of the former with half a volume of the latter, according to the principle adopted here, and a light applied, or an electric spark passed through them, or a ball of spongy platinum introduced into the mixture, they unite and form water. In the two former cases, the union is accomplished with explosive violence; in the latter case, more silently. The union of this gas with oxygen is attended with immense heat, as has already been mentioned. The safest way to work with the oxygen-hydrogen blowpipe, is to unite the oxygen and hydrogen from separate gas-holders, such as the one in diagram 4, in a common jet, taking care that the hydrogen should be in a gas-holder twice as large as that containing the oxygen, as represented in fig. 4, or as nearly as possible in that proportion, or that means should be taken to unite them in the common jet in that proportion; or if the two gases are mingled together in a reservoir in these proportions,—viz. 2 of hydrogen to 1 of oxygen,—then a safety tube should be used to pass them through, like that represented in fig. 11. Through such a tube, filled

Fig. 12.

with iron filings or copper wire, a stream of oxygen and hydrogen gas may be forced with perfect impunity from a common bladder held between the side and the arm, and by
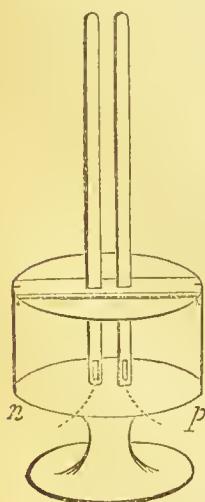
* See comparative table of weights and measures.

the pressure of the latter; thus all the phenomena of the most complex oxy-hydrogen blowpipe may be elucidated. From $a$ to $b$ the tube is supposed to be filled with copper or iron filings, $c$ is the orifice at which the gas is burned.

Hydrogen combines with numerous bodies, forming a remarkable series of compounds. Its compounds with oxygen are the protoxide, or water; the peroxide, or oxygenated water, and probably ozone. It is remarkable that although itself perfectly innocuous to animal life, so that it may be respired with impunity, many of its compounds are possessed of singularly powerful physiological properties; thus, ammonia, its compound with azote, is a very powerful gas, most destructive of animal life. Its compounds with chlorine, sulphur, carbon, arsenic, cyanogen, &c., are remarkably destructive; and there seems good ground for conjecturing that some of the subtile animal poisons, which play so important a part in the development of disease, are compounds of hydrogen, or into which this gas in some measure enters.

Hydrogen is, even more than oxygen, insoluble in water, which does not appear capable of dissolving more than $1\frac{1}{2}$ per cent of it. Like oxygen, it has not yet been liquefied.

Protoxide of Hydrogen, Water.—Eq. 9. Formula $HO$; sp. gr., as steam, 622; to air as 1,000; as water, 1.

In the formation of water the half volume of oxygen and the volume of hydrogen that it contains are condensed into one volume of steam or watery vapour. The theoretical specific gravity of steam, therefore, will be found by adding the specific gravity of hydrogen to half the specific gravity of oxygen. When water is cooled downwards, it does not regularly contract as it cools; but, on being cooled below 40°, it begins to expand until the temperature of 32°, when it suddenly expands in freezing with such a force as to be capable of bursting enormously strong vessels—an effect which is supposed to be due to the crystallisation of the ice.

The decomposition of water is best effected by means of galvanism. If the opposite poles of a sufficiently strong galvanic battery are brought, by means of wires suitably disposed, in contact with water, the water will be decomposed, its hydrogen will appear at the wire connected with the zinc, and its oxygen at that connected with the copper, and the gases may, by means of such an arrangement as is here represented, be collected as in fig. 12.* Steam passed over red hot iron is decomposed and hydrogen evolved; but what is very remarkable is, that if hydrogen is passed over heated peroxide of iron, the oxide is decomposed and water re-formed.

But, in the same way, water is decomposed by heated platinum at a very high temperature; yet oxygen and hydrogen combine, as in the flame of the oxy-hydrogen blowpipe, at an equally high or higher temperature.

* Afterwards the gases may be mixed together, an electrical spark passed through them as in the electrical eudiometer in Fig. 16, and reunited in the form of water.

The gravity of water is the unit to which the densities of all liquid and solid bodies are referred. It is 1, and at 60° is 815 times heavier than air. According to Gay-Lussac, the act of solution of bodies in water is always accompanied with production of cold; but the formation of a definite hydrate with a body, *i.e.*, a compound of water, is attended with evolution of heat.

Of late the combinations of water with acids and alkalis have been regarded as genuine compounds. It is sometimes easy to discover that a base transported into the greater number of salts, forms a substitute for a certain quantity of water. Thus, when baryta does not form anhydrous salts, it contains a single eq. of water. It is the same with lime, and the lime, with one eq. of water, differs entirely from the anhydrous lime as a base. Oxide of copper, $CuO,HO$ differs as a base entirely from the anhydrous oxide. It is the same with acids. There are two compounds of oxalic acid and water, one $C_2O_3,HO$, the other $C_2O_3,3HO$. The latter always exists in solutions of oxalic acid and in water. Now when oxalic acid combines with the hydrate of potass, the latter loses its water, but the oxalic acid only loses two of its equivalents, and we get the neutral oxalate of potass, $KO,HO,C_2O_3$; when this is heated it parts with an equivalent of water, which, in the free state, the oxalic acid never abandons, and becomes $KO,C_2O_3$. Here then the KO is instead of the original HO.

The dissolving power of water furnishes one of its most remarkable properties. When water exercises its dissolving power on substances, its first effect is to alter or abolish their physical properties. Solids and gases dissolve in the water, and disappear in it, communicating, however, their colour to the latter. In order to judge of the new influences or agencies which bodies thus dissolved acquire, beside the cases referred to already, we may take, as an illustration, such facts as the following :—Sulphurous acid and oxygen may be mixed together in the dry state without effect; but let water intervene, and they combine to make sulphuric acid. If a solution of chloride of antimony, or nitrate of bismuth, is thrown into water, it is instantly decomposed— the difference between the solubility of its constituents causing this separation, the acid remaining in solution, and the insoluble oxide being thrown down.

The dissolving power of water is one of the greatest influences in nature. By the gases it absorbs from the atmosphere, and the solids it removes from the earth, it supplies both organic and inorganic nutriment to plants, and a great portion, probably, of the inorganic nutriment of animals. It wears down mountains, and fills plains with the detritus forming soil.

The waters found in nature are thus classed :—Rain water or snow water, spring water, river or lake water, mineral water, and sea water. The first is nearly pure when collected far from towns, and is insipid from the absence of the salts usually found in spring water. It contains carbonic acid, and sometimes traces of nitric acid and ammonia. Solutions of nitrate of silver, nitrate of baryta, and oxalate of ammonia, do not affect it—tests which are resisted by very

few natural waters. Distilled water is nearly similar to rain water. Spring water contains salts ; when the amount of these much exceeds 40 grains to the gallon, the water may be said to become a mineral water. River and lake waters generally contain fewer salts than spring waters, and more organic matter, on account of the amount of surface water they receive. If river water contains much vegeto-animal matter, it has been considered apt to engender endemic dysentery. As the sea contains all the soluble matter which water can collect from the surface of the globe, and as the sand is the insoluble residue, it follows that the sea and the sand must be the complements of each other, and together represent the composition of the surface of the earth. The organic matter brought into the sea by rivers is consumed, doubtless, in the support of the vast amount of life which the sea contains.

PEROXIDE OF HYDROGEN.—Eq. 17, $HO_2$. This substance is a liquid.
When nitrate of baryta is calcined, and a stream of oxygen gas passed over the product, heated to redness in a porcelain tube, a binoxide of barium is obtained ; and as acids unite to form the salts of baryta with the protoxide of barium or baryta, it follows that, when peroxide of barium dissolves in a weak acid, oxygen gas is given off, and a salt of baryta formed. The binoxide then is to be dissolved in weak muriatic acid, and as the oxygen escapes from it, it is dissolved in the water associated with the muriatic acid. Afterwards the baryta is removed by sulphuric acid, and more binoxide dissolved, until the solution is saturated with oxygen. What muriatic acid remains at last is removed by sulphate of silver, and the sulphuric acid of this by solid baryta.
The principal phenomena connected with this body are, the extremely facile decompositions which it undergoes and *causes*. Many metallic substances, metals, and oxides decompose it instantly by simple contact, sometimes with great evolution of heat, and in some cases peroxides are formed. But in other cases the decomposition is effected without any change on the part of the decomposing agent ; while in other instances, as, for example, the oxides of gold and silver, the oxygen itself of the oxide goes off along with that of the peroxide. This substance possesses powerful bleaching properties.

### OZONE.

There is some difficulty in deciding where this substance should be put ; by some it is regarded as oxygen in an allotropic state, or as a peroxide of hydrogen.
Ozone is formed when electricity is discharged into the air, when water is decomposed, and in every instance when phosphorus is allowed to act on moist air at ordinary temperatures. It is best prepared by putting a short stick of phosphorus, well scraped, into a two-quart bottle, with as much water at the bottom as will half cover the phos-phorus. The mouth of the bottle should then be slightly closed, and the bottle set aside. A column of thin smoke will almost instantly

begin to arise from the phosphorus, which is luminous in the dark. *
Ozone may almost immediately be detected if a piece of paper steeped
in a mixture of iodide of potassium and starch be put into the bottle,
the starch becoming blue. When air much charged with ozone is
inspired, it becomes highly poisonous. Small animals put into it die;
and it acts as a powerful irritant to the air passages. As ozone, a
colourless gas, is chiefly recognisable by this property, it has led to
some very curious speculations. By many, its presence, in excess or
diminution, is supposed to be capable of explaining many conditions of
the air, which produce disease. Its smell is precisely similar to what
is produced when a powerful electro-pneumatic machine has been long
worked; and it is said that the operators in such cases experience
symptoms not dissimilar to those of influenza.

### 3. NITROGEN, N.

Eq. 14 ; sp. gr. 0·972 ; combining measure, 1 volume □.

Atmospheric air consists of 77 per cent. by weight, and nearly 80
per cent. by measure of this gas, which can be most easily prepared
from this source by abstracting
the oxygen. This is best
done by burning some phos-
phorus in a bell jar over
water, thus, as in the fig. (13).
A little phosphorus is put
into the cup, supported on a
pedestal and kindled, and as
the phosphorus absorbs all
the oxygen, if in sufficient
quantity, the water now in
the jar absorbs the phosphoric
acid formed, and the white
fumes gradually disappear. By
transferring the gas into jars
two or three times through
water, it is freed of the
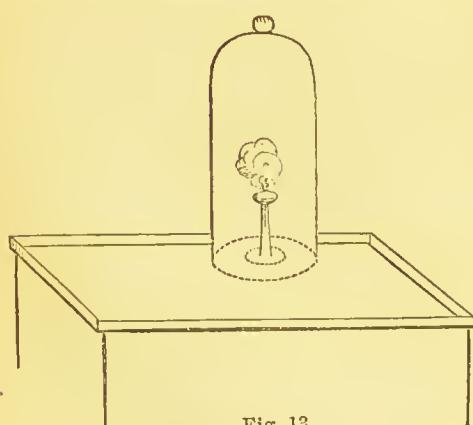


Fig. 13.

whole phosphoric acid, and nitrogen is obtained quite pure. There
are other modes, but this is quite sufficient. This gas is very slightly
soluble in water, and is chiefly known by its negative properties,
although its compounds are a sufficiently remarkable class of bodies.

The only element with which nitrogen enters into direct combi-
nation is oxygen. It combines with this element when electricity is
passed through a mixture of the gases. With hydrogen it forms
ammonia. It combines with some metals directly and forms nitrides.
Its combinations with oxygen form a beautiful series—$NO$, $NO_2$, $NO_3$,
$NO_4$, and $NO_5$. The atmosphere is a mixture.

It is incombustible and a non-supporter of combustion, respirable

* After a few hours the phosphorus should be taken out, and the
bottle well washed to free it from phosphorous acid.

except from its excluding oxygen, and in atmospheric air it seems useful chiefly as diluting the latter. In organic chemistry nitrogen plays a very important part; and the articles of food of which it forms a portion form a class different from those which do not contain it, and more concerned with the nutrition of the essential organs of life.

PROTOXIDE OF AZOTE, NO.—Eq. 22; sp. gr. 1·524; combining measure, 1 vol. $\square$.

This gas is best obtained by heating the nitrate of ammonia in a retort. The nitrate of ammonia is a compound of 1 eq. of nitric acid, and one of ammonia. When the salt is heated, it is first melted in its water of crystalisation, then it is decomposed, and resolved into protoxide of azote and water, thus—$NH_3, HO, NO_5 = 2NO + 4HO$; or upon the ammonium theory $NH_4O, NO_5 = 2NO + 4HO$. As a good deal of steam is given off, the beak of the retort should at first be put into a small cup with a little water; that on the disengagement of all the water or steam, when the actual decomposition of the salt is just commencing, water may not enter the retort in quantity from the pneumatic trough. As soon as it is found that the gas is coming off, it may then be collected in the same manner as hydrogen.

The gas is colourless, has a sweet taste, powerfully supports combustion, has been liquefied by a pressure of 50 atmospheres (see atmospheric air), and has been solidified by extreme cold. The extraordinary physiological properties of the intoxicating gas are well known.

BINOXIDE OR DEUTOXIDE OF AZOTE, $NO_2$.—Eq. 30; combining measure, 2 vols. $\square$; sp. gr. 1·0416.

Here one vol. of oxygen (2 half volumes) is united with one whole vol. of azote without condensation, consequently the specific gravity of the gas by theory will be found by adding the specific gravity of oxygen to that of nitrogen, and dividing the sum by 2.

The gas is obtained by dissolving copper in nitric acid. Such an apparatus may be employed as that used to prepare hydrogen. One part of strong nitric acid to three of water should be used. The decomposition which takes place is as follows—$3Cu + 4NO_5 = 3[CuO, NO_5] + NO_2$. That is to say, three equivalents of nitrate of copper and one of the deutoxide of azote are formed. The water takes no part in the decomposition, but only facilitates the action. The gas escapes, and can be collected over water. This gas will not support the combustion of any body that has not a very great attraction for oxygen: for instance, phosphorus introduced in a state of combustion will burn in it. Its principal property is the forming of a peroxide of azote $NO_4$, when it comes in contact with atmospheric air. As the peroxide is a most irritant substance, this is the reason why the deutoxide is irrespirable, because it would form this gas if introduced into the lungs. This gas is also called nitric oxide.

NITROUS ACID, $NO_3$.—Eq. 38; sp. gr. 1·52. This compound is also called hyponitrous acid. It is prepared by several processes. It is

only necessary to mention here the process by mixing one volume of oxygen and four volumes of nitric oxide, and cooling the mixture down to —4°. It is a very volatile liquid of a greenish blue colour. It is readily decomposed into nitric oxide, and the next compound, the peroxide of azote, thus—2 eq. $NO_3 = NO_2 + NO_4$.

PEROXIDE OF AZOTE, $NO_4$.—Eq. 46; also called hyponitric acid, and formerly nitrous acid; combining measure, 2 vols. ☐☐
This gas is formed whenever nitric oxide comes into atmospheric air, or in contact with oxygen, and if extreme cold be employed during the union, the compound will be formed as a liquid at − 4°. It is colourless at that temperature, and is a white solid at—40°. It exists in the common nitric acid of commerce, and its red fumes are often seen in processes where nitric acid is concerned.

NITRIC ACID, $NO_5$.—Eq. 52. This acid has been formed by the direct union of its constituents. If nitrogen and oxygen be mixed together in the proportion of 1 volume of the former to $2\frac{1}{2}$ volumes of the latter, and a series of electric sparks passed through the mixture, over water, and especially over solution of potass, nitric acid is formed. It is usually formed, however, by the action of sulphuric acid on nitrate of potass or soda. For this purpose, an apparatus, such as is represented in Fig. 14, is to be used to condense the acid.
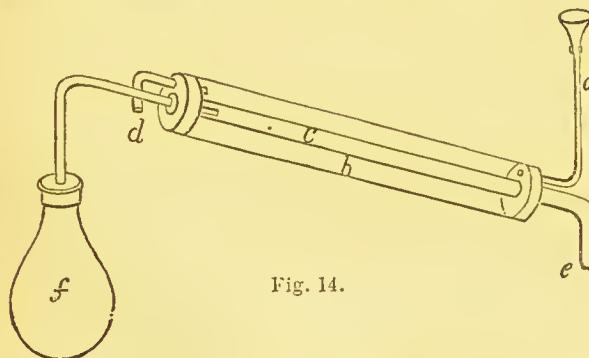


Fig. 14.

Fig. 14 represents a kind of condenser very useful in distillation. $f$ is the flask delivering the vapour to be condensed; $b$, a tin tube, supplied with water through the funnel $a$; $c$ is an interior tube of stoneware or glass, into which the vapour passes, and where it is kept surrounded by the water in $b$; $e$ is the outlet of this, whence the condensed fluid can be received in a proper receptacle; $d$ is the outlet tube for the water of $b$; a stopcock from a cistern can be caused to regulate the supply of water through $a$.

The quantities used are in the proportion of two equivalents of sulphuric acid to one of nitrate of potass, the object being to expel all the nitric acid; and this is best done when an excess of sulphuric acid is used. A quantity of nitrate of potass is put into a retort, and an equal weight of sulphuric acid poured on it.* Heat is then applied, and the nitric acid is distilled over into the receiver, which is kept cool, as

* In general, when a powder is mixed with a fluid, for a process like the present, the powder should be put into the fluid, especially if it is heavy. This is not material in the present case.

shown in Fig. 15, by the application of a freezing mixture; or the acid is condensed by the refrigeratory, as represented in Fig. 14.
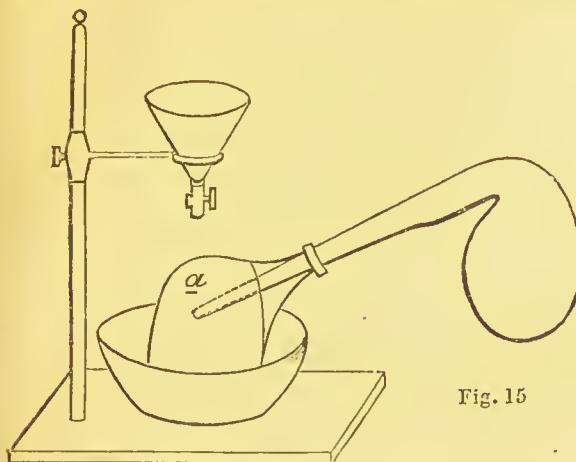


Fig. 15 represents a convenient mode of distilling, in such a case as nitric acid, when it is merely necessary to illustrate the preparation. The funnel with a stopcock regulates the supply of water, and a rag $a$, over the receiver keeps it moist and cool.

Fig. 15

$KONO_5 + 2[HO,SO_3] = KOSO_3$, $HOSO_3 + NO_5HO$; or, one equivalent of nitrate of potass, and 2 of hydrate of sulphuric acid (sulphate of water) are equal to one of sulphate of potass with one of hydrate of sulphuric acid, and one of nitric acid and water.

On the large scale, nitric acid is prepared by distillation from large cast-iron retorts, and the product is condensed in earthenware vessels. The specific gravity of the strongest acid that can be prepared at 60° is 1517 or 1520. At this point it is a compound of the constitution represented by the formula $HONO_5$. When heated, it partially undergoes decomposition, yielding oxygen and peroxide of azote, or oxygen and azote, according to the amount of heat to which it is exposed. It freezes at 40°, and boils at 184°. There appears to be another somewhat definite hydrate, of sp. gr. 1424, which contains 4 eq. of water. This acid boils at 250°. This tendency to combine with 3 eq. of water is manifested by the compounds of other bases with nitric acid. Thus, the 2nd nitrate of water would be $HONO_5$, $3HO$; and we have prismatic nitrate of copper, $CuO$, $NO_5$, $3HO$; rhomboidal nitrate of copper, $CuO$, $NO_5$, $3HO$, $3HO$.

The principal properties of nitric acid are those connected with its oxidising powers. Sulphur, carbon, phosphorus, iodine, and many other bodies, can be oxidised at the expense of nitric acid. Many of the metals, without the aid of heat, acquire oxygen from one equivalent disengaging the deutoxide and peroxide of azote, and forming oxides, with which the other equivalent of acid combines.

In the case of metals which dissolve in weak acids with evolution of hydrogen, such as zinc, ammonia is often formed; the evolved hydrogen being in the nascent state, decomposing a portion of the compounds of oxygen and nitrogen evolved, and combining with the latter. Nitric acid acts powerfully on organic matter, forming compounds with some

of them of a highly explosive character, such as gun cotton; it also corrodes the skin and coagulates, and afterwards dissolves, when the acid is in excess, albumen.

Perhaps the best test for it is its action on sulphate of indigo. A very dilute solution of this substance may be boiled without alteration, but if, when it is at the boiling point, any solution containing *free nitric acid* is added to it, the colour is instantly destroyed. Another excellent test consists in mixing the liquid supposed to contain it with oil of vitriol, and adding the solution of protosulphate of iron: this gives a rose tint. If free nitric acid be neutralised with potass, and evaporated to dryness, it gives prismatic crystals of nitre, which deflagrate on red-hot charcoal.

### ATMOSPHERIC AIR.

The composition of the air is ascertained in several modes. 1st. A stick of phosphorus may be put into a graduated jar of it over water. The phosphorus undergoes a species of slow combustion, and the water gradually rises in the jar: in 24 hours it will be thus found that the oxygen had occupied 20 or 21 per cent. of the jar. 2nd. A quantity of air is mixed with about half its bulk of oxygen, and exploded over water or mercury by means of the electric spark (see Fig. 16), and the diminution of bulk observed: one-third of it will be oxygen.

Fig. 16 represents the eudiometer of Dr. Ure. It is a bent tube containing mercury. At the closed end two wires are soldered in. This end is graduated. By a little manipulation the jars are introduced into the closed end which is graduated. The mercury remains at the bottom of the closed end, and in the open tube. The electric spark is passed from A to B, and after the explosion, the column of mercury rises in the closed end, and, of course, falls in the open one. The rise measures the amount of contraction. A simple straight tube with the wires is Volta's eudiometer.



Fig. 16.

Air, besides containing oxygen and nitrogen, contains carbonic acid in the proportion of 1 to 2,000; it is this carbonic acid which is the grand source of the carbon of the vegetable world. Plants absorb the carbonic acid and fix the carbon in their tissues, and evolve the oxygen. Thus the digestion of plants balances the processes of respiration and combustion by which such quantities of carbonic acid are sent into the air. There are also traces of other gases, such as hydrogen and ammonia. Doubtless, infinitesimal quantities of various compounds exist, and some which may exert vast influence over health and disease, although they may be in inappreciable quantity.

The pressure of the atmosphere at the level of the sea is about 30 inches; *i. e.* it is able to support a column of mercury of that height in a barometer tube—a weight equal to 15 pounds on the square inch of surface. Hence that is called the pressure of the atmosphere. The effect of atmospheric pressure on the vaporisation of bodies is shown by

the fact that water will boil on the tops of mountains at a much lower point than on plains. This led to the experiments which have reduced so many gases to the liquid form by the pressure of their own vapours. For this purpose the substances requisite to generate a gas are introduced into one end of a bent tube, and the other extremity sealed up, the gas generated reacts by its own pressure and assumes the liquid form. Little capillary tube gauges, closed at one end, containing air, are inserted in the tube, and by means of a moveable piston as it were of mercury, between the inclosed air and open end of the tube, the pressure on the air can be ascertained. Thus, if the air is forced into half its bulk, the pressure is said to be twice that of the atmosphere; if the air be forced into one-third of its bulk, the pressure is said to be equal to three atmospheres. Students often find some difficulty in comprehending how a small quantity of air imprisoned in a vessel can exert a pressure equal to that of the atmosphere; but they should recollect the perfect elasticity of the air, which reacts, like a perfect spring, with a force equal to that to which it has been subjected.

## 4. CHLORINE, Cl.

Eq. 35·5; combining measure, one vol. □; sp. gr. 2440.

This, after oxygen, is perhaps the most important of the electro-negative bodies. It is obtained from its most important compound, the hydrochloric or muriatic acid. For this purpose, the general mode of proceeding adopted is to put one part of the peroxide or black oxide of manganese along with four of muriatic acid, into a flask or retort, and heat it; and the disengaged gas should be passed through a little water before being collected or otherwise used, as in Fig. 17. The theory of the process is, that oxygen

Fig. 17 represents a wash-bottle, which may be used in preparing chlorine; a bent tube from the flask generating the gas passes into it.

Fig. 17
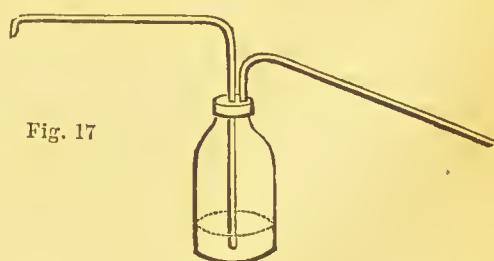


is liberated from the peroxide of manganese as in the process for preparing oxygen by means of the action of sulphuric acid on the same peroxide, i. e., the peroxide or binoxide is converted into the protoxide, with which an equivalent of muriatic acid combines to form the hydrochlorate of protoxide of manganese or muriate of manganese; while the equivalent of oxygen set free decomposes another equivalent of hydrochloric acid, taking its hydrogen to form water, and liberating the chlorine. Thus, $2MnO_2 + 2ClH = MnO, ClH + Cl + HO$. But every hydrochlorate may be represented as a compound of chlorine with the base. Thus, MnO, ClH may be represented as MnCl, HO.

The small quantity of water through which the gas is passed is to remove any hydrochloric acid that may escape. The gas must be collected over water, which should be of the temperature of 100°. The reason is, that water at 60° dissolves twice its volume of the gas; and as mercury combines with chlorine the gas cannot be collected over water. Sometimes, instead of the process described, common salt, or chloride of sodium, manganese, and sulphuric acid are used. In this case the sulphuric acid liberates muriatic acid from the hydrochlorate of soda or chloride of sodium, $NaCl$, $HO$, or $NaO$, $ClH$, and oxygen from the manganese, as in the process for obtaining oxygen. This oxygen decomposes the hydrochloric acid in the way ust described, and chlorine is evolved.

On the large scale in the manufacture of bleaching-powder, this latter process is sometimes adopted, and a large leaden retort is used for the purpose; but as that manufacture is generally carried on in alkali manufactories, and as the first manufacture of carbonate of soda consists in the decomposition of muriate of soda (common salt) by sulphuric acid, and during this process there is great disengagement of muriatic acid, which requires to be condensed in condensers, to prevent its doing mischief to the surrounding vegetation, or affecting the comfort of the surrounding population, it is the more common practice to use this acid for making bleaching-powder.

Chlorine, when collected, is a gas of a yellowish green colour, but can be condensed into the liquid form by a pressure of four atmospheres. Its solution in water is decomposed by light, water being decomposed, hydrochloric acid formed, and oxygen set free.

Chlorine unites with hydrogen in equal volumes to form muriatic or hydrochloric acid. The gases can be mixed in the dark without combining; but they may be made to combine by the approach of flame, by spongy platinum, the electric spark, or even light.

Chlorine acts upon many hydrocarburets. A good illustration is afforded by dipping a piece of paper steeped in turpentine in a bottle of chlorine—the paper is ignited, and a smoky flame arises, which is succeeded by great deposition of carbon. The explanation is, that the hydrogen, having most affinity for chlorine, is consumed, and thus the greater part of the carbon is deposited. Several metals, as antimony and others, put in fine powder into chlorine, take fire, and chlorides are formed.

The physiological properties of chlorine are very remarkable: the gas, when inhaled, produces intense irritation of the fauces. It has the power of destroying miasmata, and bleaches powerfully.

In bleaching, the cloth, well washed, is boiled in lime-water, then in solution of caustic soda. It is then steeped in a weak solution of chloride of lime, and then in a weak solution of sulphuric acid, which sets free the chlorine. These processes are repeated until bleaching is effected. The cloth is then well washed, to get rid of the last traces of sulphuric acid.

The chief compound of chlorine is the hydrochloric acid; its compounds with oxygen are $ClO$, or hypochlorous acid, $ClO_3$ chlorous acid,

$ClO_4$ or peroxide of chlorine, $ClO_5$ or chloric acid, and $ClO_7$ hyperchloric acid. Chlorine forms a most extensive series of compounds, combining with all the other elementary bodies; and, in organic chemistry, its range of combination is almost equally extensive.

HYDROCHLORIC, OR MURIATIC ACID, ClH.—Eq. 36·5, combining volume, 2 vols. ☐☐, sp. gr. 1269.5.

As this gas is composed of a volume of chlorine and one of hydrogen, united without condensation, its specific gravity will be found by dividing the sum of the specific gravities of its constituents by 2. It is best prepared by decomposing its almost universal compound, the hydrochlorate of soda, or chloride of sodium, by muriatic acid. An apparatus like that represented in fig. 18, may be used to perform the
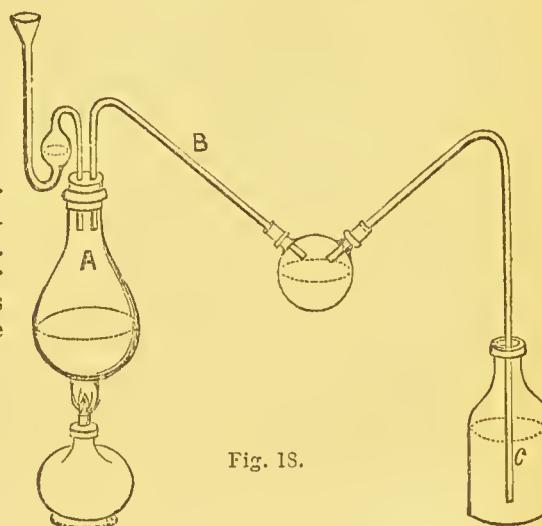
Here A is the flask for generating the gas, provided with a safety tube. B is a tube, and globular receiver; and $c$ represents the water into which the gas is finally passed.



Fig. 18.

process on the small scale: 3 parts of common salt, 5 of oil of vitriol, and 5 of water may be taken. The oil of vitriol, previously mixed with 2 of the water, and allowed to cool, is poured upon the salt in the retort, the remaining 3 parts of water are put into the bottle, or receiver. On applying heat to the retort, the gas comes readily off, and is condensed by the water in the receiver. One explanation of the process is, that hydrochloric acid is simply disengaged from the muriate by the superior affinity of sulphuric acid. Another is, that the salt exists as chloride, and in that case NaCl, $HO+SO_3$ are the substances involved in the decomposition, then the eq. of water is decomposed; its hydrogen goes to the chlorine to form hydrochloric acid, its oxygen to the sodium to form oxide of sodium, with which the $SO_3$ combines, and we get the above formula, $=NaOSO_3+ClH$.

The strongest liquid acid has a specific gravity of about 1200, and contains 6 equivalents of water to 1 eq. of acid. If this acid be exposed to the air, it fumes and loses acid so as to come to consist of 1 eq. of

acid to 12 of water; it has then a sp. gr. of 1119.   The acid made in the ordinary way has generally a sp. gr. of 1170.

On the large scale, there is an abundant source of muriatic acid in the manufacture of alkali.   Many manufacturers are not at the trouble to collect the muriatic acid which is disengaged, as stated under the head of chlorine, when, in the first stage of that process, muriate of soda is decomposed by sulphuric acid.   Of the enormous quantity of acid disengaged in this way some idea may be derived from the fact, that many manufacturers decompose 100 tons or more of muriate of soda weekly.   When this gas was allowed, as during the first years of the alkali manufacture, to escape into the air, great mischief was done to vegetation, to household furniture, and, in some instances, to health.   In order to correct this, condensers were erected, into which the fumes were made to pass on their way from the furnace to the chimney.   These condensers were formed on the plan of a still, being stone towers, consisting of two compartments, filled with coke, through which water was made to trickle.   In this way the condensation is now so complete, that complaints of the injury done by this very important manufacture are comparatively rare.

Muriatic acid is obtained in the gaseous form by heating it in a small retort, and collecting it over mercury.   If a little water be introduced into a jar of it so collected, the gas is absorbed with the greatest rapidity, the water condensing as much as 418 times its volume.*   The hydrochloric acid of commerce generally contains sulphuric acid, from which it may be freed by diluting it to sp. gr. $1.1$, and then adding chloride of barium and redistilling the acid—the sulphuric acid remains behind as sulphate of baryta.   When hydrochloric acid is mixed with half its bulk of nitric acid, it forms *aqua regia*, so called because it has the power of dissolving gold, owing to the liberation of some chlorine from the oxygen of the nitric acid combining with some of the hydrogen of the ClH.

HYPOCLOROUS ACID, ClO.—Eq. $43.5$; sp. gr. of vapour, 2977; combining measure, 1. vol. ☐.

This substance is obtained in the liquid form by agitating water and red oxide of mercury in a bottle of chlorine vapour.   Two equivalents of the oxide of mercury and two of chlorine are necessary for the process.   One of the equivalents of oxide of mercury gives an equivalent of oxygen to the chlorine, and forms an equivalent of hypochlorous acid, which is taken up by the water leaving another atom, while the remaining chlorine combines with the mercury.   There is thus one equivalent of chloride of mercury and one of oxide of mercury, which unite and form the oxichloride.   Or $2\ HgO + 2Cl = HgCl, HgO + ClO$.   The solution of hypoclorous acid is then to be decanted.   The acid solution can be heated, and the gas evolved collected in a smaller quantity of water than is requisite for its first formation; and it can be evolved from this in the gaseous form by introducing fragments of some very

* Muriatic acid gas can be liquefied by a pressure of forty atmospheres.

deliquescent salt into the jar containing it, over mercury. The gas is of a deep yellow colour, easily exploded by heat, is very soluble in water, which takes up 100 times its volume; does not redden litmus, and bleaches powerfully. With bases it forms hypochlorites. The chief interest they possess arises from their bleaching properties. In the chlorides of the alkalies and alkaline earths they exist, combined with a chloride of the base. They may be regarded as intermediate steps between the formation of a chlorate and chloride, the ultimate results of the action of chlorine on these oxides. Thus, if an equivalent of water be decomposed when chlorine is passed into an alkaline solution, for 1 eq. water decomposed there is an atom of hydrogen for one eq. of chlorine, and of oxygen for another, and thus we have $ClO$ and $ClH$ obtained; the one will combine with one equivalent of the base, forming a hypochlorite, and the other with another equivalent forming a hydroclorate or chloride; but if the solution be concentrated or hot, the decomposition goes on till of 5 equivalents of water decomposed, the whole oxygen goes to one eq. of chlorine, forming $ClO_5$ and the 5 of hydrogen to 5 of chlorine, forming 5 $ClH$, which unite with as many equivalents of base.

CHLOROUS ACID, $ClO_3$ and HYPOCHLORIC ACID, or PEROXIDE OF CHLORINE $ClO_4$, are products of the action of various acids on the chlorate of potass. They are both highly explosive substances, and have no particular use.

CHLORIC ACID, $ClO_5$, eq. 75·5, may be obtained in a concentrated, although not anhydrous form, by decomposing solution of chlorate of baryta by an equivalent proportion of sulphuric acid, which throws down the sulphate of baryta, and leaves chloric acid in solution. The solution can be concentrated by evaporation in the vacuum of the air-pump.* This substance, containing a large quantity of oxygen and its elements, from their similar electro-negative position, being only held together by a loose affinity, parts readily with its oxygen; hence its salts, the chlorates, form very powerful explosive compounds. Phosphorus, sulphur, and other inflammable substances, readily detonate on being mixed with the chlorates when friction is applied. The chlorates do not bleach; when treated with sulphuric acid, they yield a yellow gas. Perchloric acid $ClO_7$, and chloroperchloric acid $2ClO_7$, $ClO_3$, are of no particular moment.

CHLORIDE OF NITROGEN is a highly explosive compound, formed by the action of chlorine on solution of muriate of ammonia. Its composition is not very well known.

## 5. BROMINE, Br.

Eq. 71·26; sp. gr. of vapour, 5593; combining measure, ☐. This body is found chiefly in the sea and in marine productions, or in salt springs, where it is almost always associated with chlorine, and sometimes with iodine. It is obtained from the bittern,

* See Potassa.

or mother-liquor of the sea water, or of salt springs, in which, after the separation of the greater portion of the salts by crystallisation, the high solubility and small quantity of the bromides enables them to remain in solution. Chlorine gas is first passed through such mother water. It evolves bromine, which colours the liquid of an orange yellow. When the colour has ceased to become deeper, the liquid is then agitated in a bottle with ether, which dissolves the bromine, and floats as a red coloured liquid at the top of the vessel. This etherial solution of bromine is then to be removed, either by decanting it carefully, or by means of a syphon. Potassa is added to this, which causes the formation of the bromate of potass, and bromide of potassium, from which bromine may be obtained, by heating the crystals of these salts with peroxide of manganese and sulphuric acid, by a process analogous to that for obtaining chlorine from muriate of soda, and sulphuric acid and peroxide of manganese.* Water should be put into the receiver.

Bromine is a deep colored red liquid, of sp. gr. 2·966. Its odour is very powerful, similar to that of chlorine. It is volatile at the ordinary temperature of the air, boils at 116.5, and freezes at about— 7 deg. It is slightly soluble in water, more so in alcohol, upon which it acts. Its best solvent is ether. It bleaches like chlorine, and acts similarly on oily and organic substances; it also combines like chlorine with many metals, occasioning combustion at the time; acts powerfully on organic substances, and hence is a powerful corrosive poison.

Its principal compounds are hydrobromic and bromic acids; but there is strong reason for believing that it forms other compounds with oxygen besides the latter; it besides, in all its chemical relations, closely imitates chlorine, and like it forms a vast number of compounds, both inorganic and organic. In organic chemistry, especially where a compound of chlorine with any radical exists, the existence of an analogous compound of bromine may pretty safely be predicted.

HYDROBROMIC ACID, HBr, or BrH, writing the symbol in the ordinary way for muriatic acid.†—Eq. 79·26; combining measure, one vol. ⬜.

This gas may be prepared by several processes, all analogous to processes for preparing the analogous compound of iodine, the hydriodic acid. The 1st process consists in bringing bromine very carefully in contact with phosphorus in water, cut into chips, and covered with pounded glass, and applying a gentle heat; the water is decomposed, and phosphoric and hydrobromic acids formed, the phosphorus taking the oxygen and the bromine the hydrogen; the hydrobromic acid gas is formed and can be collected over mercury or absorbed by water, like the hydrochloric, which it closely resembles in its properties. Or 2nd, sulphuretted hydrogen gas may be passed into bromine under water; the bromine takes the hydrogen from the

* It is better to heat the crystals before mixing them with sulphuric acid and manganese; by this means the bromate is converted into the bromide.

† The most correct symbol for the latter would be HCl, instead of ClH

sulphur, and hydrobromic acid is formed; afterwards the sulphur is removed by filtration, and the excess of hydrosulphuric acid by heat. Or 3rd, a solution of bromide of barium may be carefully decomposed by an equivalent portion of sulphuric acid; sulphate of baryta is formed, and hydrobromic acid remains in solution. Bromic acid, $BrO_5$, may be produced like chloric acid from bromate of baryta, but has not been isolated.*

## 6. IODINE, I.

Eq. 126·36; sp. gr. of vapour, 8707; combining measure, ☐ 1 vol.

Iodine exists in the sea, and in marine productions, along with chlorine and bromine. It exists also in the oil of the cod, and in the flesh of several fishes, and in many salt springs. It is also known to form one mineral, an iodide of silver. It is generally obtained from the bittern of kelp, or barilla. These names are given, the former to the ashes of sea-weeds obtained on our coasts, the latter to such as are manufactured in the Mediterranean. The sea-weed is collected, dried, and burned in a shallow pit. The ashes are run together by the heat, and form a compact mass. The object of the manufacture of iodine at present is, to obtain, not merely the iodine, but the salts of soda, and especially of potass, which the kelp contains. For this purpose the kelp is broken to pieces, and allowed to steep in water, either cold or hot, until its soluble matter is extracted. This water is then run off and boiled down. As the liquid boils down, the soda-salts crystallise first, and are removed; afterwards the liquid is run into pans, where, on cooling, a quantity of crystals of chloride of potassium are deposited. The mother liquid is then treated with sulphuric acid, and mixed with binoxide of manganese in a lead retort, and heat is applied. The iodides are decomposed in the same way as chloride of sodium is decomposed, by the same substances; and iodine is sublimed into properly constructed receivers. It is afterwards purified. The process may be illustrated by heating the hydriodate of potass with sulphuric acid and black oxide of manganese in a tube, when the deep violet fumes of iodine will be evolved.

Iodine is a solid, in the form of dark blue or purple crystalline scales. Its density is 4·948. It melts at 225°, and boils at 347°. The vapour presents a splendid violet colour. Water only dissolves $\frac{1}{7000}$ part of it; but it is soluble to a much greater extent in solutions of iodides. Iodine is soluble in alcohol and ether, and does not act like bromine on the former.

Iodine has a great power, when administered medicinally, of permeating the tissues, and its presence can be easily ascertained; all that is necessary is to take some of the tissue supposed to contain it, and add some sulphuric acid with some nitric acid to it in a flask, and

* The best qualitative tests for bromides in solution is the solution of chloride of gold, which gives a splendid red colour. The bromide of silver is analogous to the chloride, but of a light yellow colour; when heated with bleaching powder and chlorine, it affords red vapours of bromine.

then suspend a piece of starched cotton in the neck of the flask, lightly by a cork, when, after a time, the cotton will be darkened if iodine be present. This dark blue compound of iodine and starch offers a very ready mode of detecting iodine qualitatively. It has been discovered lately, that where the quantity of iodine is small at any rate, sulphuric acid does not act, if pure; but the acid of commerce generally contains some nitric acid. The theory of the action is this:—iodine, in combination, has no action on starch. It must be liberated; which is effected by the sulphuric and nitric acids, or by the latter alone; and the hydriodic acid, having its hydrogen oxidised by the oxygen of the nitric acid, iodine is set free, just as chlorine is in *aqua regia*. The iodide of silver is obtained in the same way as the chloride and bromide, and has analogous properties. Heated with bleaching powder and muriatic or nitric acid, it evolves iodine.

The combinations of iodine are not so analogous to those of chlorine as to those of bromine; and its range of affinity is not quite so extensive as that of these elements. Nevertheless, it combines with most of the simple bodies, and forms a numerous class of compounds in organic chemistry. The most important of its compounds are those with hydrogen and oxygen, or IH hydriodic acid, and $IO_5$ iodic acid, and $IO_7$ periodic acid.

HYDRIODIC ACID, IH.—Eq. 127·36, is prepared by processes precisely similar to those for preparing hydrobromic acid. It is a gas very soluble in water. The solution is decomposed by oxidising agents; with evolution of iodine. Its compounds with oxides may be represented, like the hydrochlorates, as, taking the case of hydriodate of potass, KOIH, or KI+HO, iodide of potassium and water.

IODIC ACID, $IO_5$, eq. 167·36, may be prepared in small quantity by digesting iodine in nitric acid; with the aid of heat, the iodine is oxidised by the nitric acid, and deposited in crystals on the cooling of the liquid.

To prepare iodic acid in quantity, iodine is suspended in water, and a stream of chlorine passed through it; the result is the formation of chloride of iodine. When carbonate of soda is treated with this, the carbonic acid is driven off, and, by the disposing affinity of the chlorine and iodine forming salts with the soda, water is decomposed; and the chlorine having the stronger affinity for hydrogen, being more electro-negative than the iodine, takes the electro-positive hydrogen, and leaves the oxygen to the iodine; we have then the formation of hydrochlorate of soda and iodate of soda, 5 eqs. of the former, and one of the latter; or $5Cl+5HO+I=5ClH+IO_5$; and these equivalents of the respective acids, of course, find each an equivalent of base. The solution is filtered and treated with chloride of barium, the iodate of soda is decomposed, muriate of soda and iodate of baryta formed, which may be collected on a filter and dried. It can be decomposed by boiling with sulphuric acid and water; sulphate of baryta is formed, and the solution of iodic acid which remains is gently evaporated to

dryness. Iodic acid is very soluble in water, the solution reddens, and then bleaches litmus. It is a powerful oxidising acid. It is decomposed by sulphurous acid, and iodine liberated, as can be shown by the starch test.

The iodates closely resemble the chlorates, but deflagrate less powerfully.

PERIODIC ACID, $IO_7$, eq. 182·36, is formed by passing a solution of chlorine through a solution of iodate and a little carbonate of soda; the formation of the chloride of sodium sets free some oxygen, which goes to the iodate, forming periodate of soda, which is deposited from the solution in silky crystals. Afterwards from this a periodate of silver is formed, from which periodic acid is obtained by throwing crystals of the neutral periodate into water; half the periodic acid is separated by the water and remains in solution. This acid forms a class of salts called periodates.

## ANALOGIES BETWEEN CHLORINE, BROMINE, AND IODINE.

Many of the elementary bodies in chemistry form groups possessed of remarkable analogies, which analogies exist also in their compounds. Such are most of the isomorphous groups; but as in none are these so remarkable as in the group just named, it is worth while by way of illustration of these analogies to sum them up.

1st. The equivalent of chlorine is the smallest, then comes bromine, and that of iodine is highest.

2nd. Chlorine is a light green gas, bromine a deep red liquid, iodine a solid of an intense violet hue.

3rd. The volatility of the respective compounds in general follows the rule of the base. Hydrochloric acid is the most volatile of the three hydracids, and hydriodic acid is the most fixed. The chloride of potassium is volatile at a brown red heat, while the iodine requires a much more elevated temperature. Chloride of cyanogen is gaseous at ordinary temperatures, when the bromide and iodide of the same substance are solid. The chlorides and bromides of olefiant gas and formyl are liquid, but the corresponding iodides are solid.

4th. The compounds of bromine are frequently of a deeper hue than those of chlorine, but the compounds of iodine are the most coloured of all.

5th. The specific heats of the compounds bear the same kind of relation. Thus in the tables given by M. Regnault of the specific heats of compound bodies, the specific heats of bromides are less than those of chlorides, and greater than those of iodides.

6th. It has lately been ascertained that in endosmotic power the bromide of potassium occupies an intermediate place between the chloride and the iodide.

7th. Finally, the compounds are isomorphous, and their physical and chemical relations are all imitated by their analogous physiological and medicinal properties, those of the bromides being intermediate between the chlorides and iodides.

## 7. FLUORINE, F.

Eq. 18·70, sp. gr. of vapour, by theory, 1292, combining vol. 1, ☐.

Perhaps, in the proper order, fluorine should have preceded chlorine, as it seems to be even more electro-negative, and possessed of more powerful affinities than even that substance. Hence it is most difficult to isolate fluorine, as it acts upon so many materials that it is almost impossible to obtain a vessel capable of holding it. In short, it is very doubtful whether fluorine has yet been obtained in a separate form.

Its principal compound, the hydrofluoric acid, FH, is readily obtained by gently heating fluor spar, or the fluoride of calcium, powdered, in a leaden retort, along with sulphuric acid. The acid is given off, and may be condensed in the liquid form by means of a freezing mixture, or be distilled into a leaden receiver. The decomposition is analogous to what takes place when muriate of soda, or chloride of sodium is decomposed by sulphuric acid, substituting fluorine for chlorine, and hydrofluoric acid for hydrochloric acid. When hydrofluoric acid is brought into contact with boracic and silicic acids, it forms compounds—the terfluoride of boron and terfluoride of silicon. It is owing to this that vapours of hydrofluoric acid may be used to etch on glass. When the vapours of the terfluoride of silicon are passed into water, the silica is deposited, and hydrofluoric acid absorbed by the water. This action will be represented by the following formula :—$SiF_3 + 3HO = 3FH + SiO_3$.

When hydrofluoric acid, acting upon silicic acid, as in glass, forms the terfluoride of silicon, then $3FH + SiO_3 = SiF_3 + 3HO$.

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## 8. SULPHUR, S.

Eq. 16; sp. gr. of vapour, at 900°, 6633; combining measure, $\frac{1}{6}$th of a volume.

Sulphur exists abundantly in nature, either nearly pure or in the form of metallic sulphurets,—as of lead, iron, zinc, copper, arsenic, &c. These ores are called pyrites. It also exists extensively in nature under the form of sulphates, i. e., compounds of its principal acid with oxygen, the sulphuric acid, with various bases. Thus, sulphates of lime and baryta are extensively diffused minerals; and numerous sulphates exist in spring and mineral waters, and in the organic kingdom.

Sulphur is commonly sold as rolled sulphur, or flowers of sulphur, the former being the fused element run into moulds, the latter the same sublimed, in which form it is purer. Sulphur has a sp. gr. of 1·98. The circumstances attending the application of heat to it are curious. It melts at 234°, forming a clear, slightly coloured liquid; if heated further, the colour gets deeper, until at 482° it is of a deep brown colour. About this temperature it is also very viscid; and, run into water, it forms a tough mass, which readily takes impressions of

objects, seals, &c. Heated above 500°, it again becomes more fluid and continues so until 788°, when it boils.

Crystals of sulphur may be formed by melting a quantity in a Hessian crucible, allowing the mixture to cool until it is nearly solid; then, making a hole in the outer crust, and inverting the crucible, the still fluid portion runs out, and the remaining portion has space in which to shoot out crystals. These crystals are oblique prisms, with rhomboidal bases, while from its solutions it is obtained in elongated octohedrons. Sulphur is therefore dimorphous; and, from the changes which it undergoes in its fusion, it is also allotropic.

Sulphur is insoluble in water, and soluble in some few fluids,—as the sulphurets of carbon, turpentine, and the chloride of sulphur. When heated with many of the metals, it combines with them,—sometimes with evolution of heat and light. In its relations with bases, it closely resembles oxygen.

No less than seven compounds of it with oxygen are now enumerated:—hyposulphurous acid, $S_2O_2$; sulphurous acid, $SO_2$; hyposulphuric acid, $S_2O_5$; trithionic acid, $S_3O_5$; tetrathionic acid, $S_4O_5$; pentathionic acid, $S_5O_5$; sulphuric acid, $SO_3$.

Those only which require attention here, are the 1st, 2nd, 3rd, and 7th.

### Hyposulphurous Acid, $S_2O_2$; Eq. 48.

This acid cannot be isolated; but is obtained in combination with bases, with which it forms hyposulphites. It is most readily obtained by boiling an alkaline sulphite with sulphur. In such a case, the sulphur added takes one of the equivalents of oxygen in the sulphurous acid. Thus $KO,SO_2+S=KO,S_2O_2$. These salts have been lately found to possess the property of dissolving the chloride, bromide, and iodide of silver; hence they are employed in photography, to remove, after the impression has been produced, the excess of undecomposed chloride, bromide, or iodide, which, if it remained, would still be sensitive, and interfere with the original impression.

### Sulphurous Acid, $SO_2$; Eq. 32; sp. gr. of vapour, 2247; combining measure, 1 vol. ▢

This gas is produced when sulphur is burnt in common air; and its vapours occasion the disagreeable sensation which is experienced when this is done. It is generally prepared chemically, by heating sulphuric acid with mercury or copper in a retort. The gas is carried through a small waste-bottle, similar to that in fig. 17, in case any sulphuric acid should come over with the vapour, and then over chloride of calcium, if it is desired to have the gas dried. Sulphurous acid must be collected over mercury if it is wished to examine the gas, although it may be collected by what is called the method of displacement. In this way a very heavy gas may often be collected, by its vapour displacing atmospheric air. See fig. 19. Sulphurous acid can be collected in large quantities by heating sulphuric acid with charcoal. When an aqueous solution is required, the gas must be passed into water,

which absorbs about 50 times its volume of it at 50°.   The theory of these processes for obtaining sulphurous acid is as follows : —
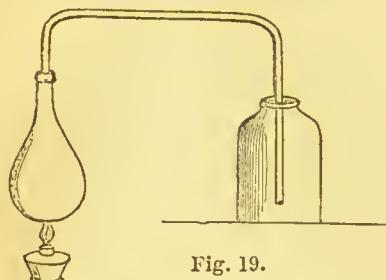


Fig. 19 represents the mode of collecting a gas by simple displacement.

Fig. 19.

When mercury and sulphuric acid are heated together, one eq. of $SO_3$ is decomposed, in order that the mercury may be oxidated, so as to be enabled to combine with another eq. $SO_3$, and form the sulphate of oxide of mercury.  Thus, $Hg + 2SO_3 = HgO, SO_3 + SO_2$.  When carbon is heated with sulphuric acid, it decomposes it, and carbonic acid and $SO_2$ are formed, then $2SO_3 + C = CO_2 + 2SO_2$.  The latter is a cheaper
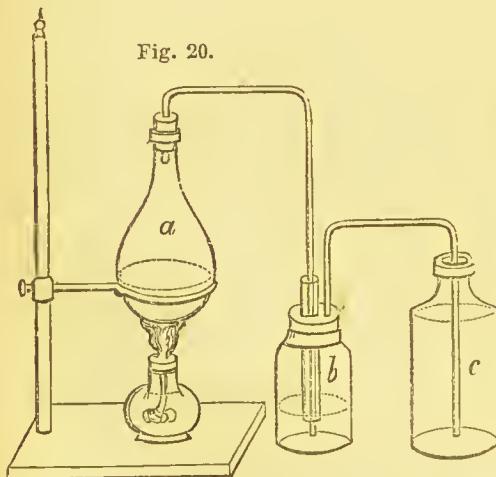
Fig. 20.



Fig. 20 represents a convenient apparatus for preparing sulphurous acid by the action of $SO_3$ on carbon.  One part of charcoal is mixed with 12 or 14 parts of oil of vitriol in the flask $a$; the first bottle $b$ contains a small quantity of water.  This bottle is to condense any excess of sulphuric acid that may be driven off.  The bottle $c$ contains a large quantity of water to condense the sulphurous acid.

mode of procuring abundance of sulphurous acid, and if a solution is required, sufficiently convenient ; the gas, however, will be mixed with much carbonic acid.  By exposing sulphurous acid to the cold of a freezing mixture, or subjecting it to a pressure of two atmospheres of its own vapour, at 60°, it assumes the liquid form.  It boils at 14° of Fahrenheit.

Sulphurous acid bleaches many organic bodies ; and the vapours are used in bleaching straw and silk.  The colours can be restored on application of a stronger acid, or an alkali.  Sulphurous acid has a strong attraction for oxygen ; it is converted by nitric acid and iodic acid into sulphuric acid—in the latter case, with evolution of iodine;

which can be tested by starch. The gas passed into a solution of nitric acid forms a solution of sulphuric acid, which can be tested by means of nitrate of baryta; if sulphuric acid be present, the insoluble sulphate of baryta will be found. This, along with the action of iodic acid, may be taken as a test for sulphurous acid.

## Hyposulphuric Acid, $S_2O_5$; Eq. 72,

is formed when binoxide of manganese in fine powder is suspended in water through which sulphurous acid is transmitted. A solution of hyposulphate of protoxide of manganese is formed thus: $2SO_2 + MnO_2 = MnO, S_2O_5$. The solution is then filtered, and mixed with a solution of the sulphuret of barium, which throws down the insoluble sulphuret of manganese, and leaves the hyposulphuric acid in combination with the baryta. From the solution of this salt all the other hyposulphates may be formed, by adding a soluble sulphate to it;—the sulphuric acid of the sulphate goes to the baryta, and the hyposulphuric acid of the baryta to the other base. Thus, take the sulphate of soda $NaOSO_3 + BaO$ $S_2O_5$, hyposulphate of baryta; these, on being mixed in solution, will produce $BaOSO_3 + NaOS_2O_5$. And hyposulphuric acid itself may be obtained by decomposing the hyposulphate of baryta with an equivalent portion of sulphuric acid, and evaporating the solution in the vacuum of the air-pump until it is concentrated to 1·367.* If it is attempted to concentrate beyond this, the hyposulphuric acid is decomposed, and resolved into $SO_2$ and $SO_3$.

Sulphuric Acid, $SO_3$; sp. gr. of vapour, 2762; combining measure, 1 vol. ☐.

This most important acid is prepared in commerce in two ways, either by the distillation of copperas, or sulphate of iron. First, water is driven off, then there is some decomposition of the salt, since sulphurous acid and peroxide of iron are formed; but one equivalent at least of sulphuric acid is driven off pure. $2FeO, SO_3 = SO_2 + Fe_2 O_3 + SO_3$. This acid is made at Nordhausen, in Germany, and is always called the Nordhausen acid; it has a sp. gr. of 1·9, and contains 2 of real acid to 1 of water. Its formula is $2HO, SO_3$. But the far larger quantity of sulphuric acid prepared is manufactured by oxidating sulphurous acid by means of nitric acid, in the enormous manufactories known as oil of vitriol and alkali works. It is necessary to bear in mind, before considering the theory of this process, that deutoxide of azote, $NO_2$, is, as has been stated, when it comes into contact with air, almost immediately converted into peroxide of azote, $NO_4$; that nitric acid is acted upon by sulphurous acid becoming peroxide of azote and $SO_3$; that both the peroxide of azote and nitrous

* Substances are dried in vacuo by placing them in the receiver of the air-pump, over some substance having a strong affinity for water. When the air is exhausted, the water in the substance to be dried rises in vapour, and it is absorbed by the article which has a strong affinity for water, above which it is placed. The vacuum is thus kept up, more watery vapour rises to be again absorbed, and so till it is all removed.

acid, $NO_3$, perform various decompositions, two equivalents of the former being capable of being resolved into one of nitric acid, and another of $NO_3$ nitrous acid—thus, $2NO_4HO = HONO_5 + NO_3$; while the nitrous acid itself is sometimes resolved by water into nitric acid, water, and deutoxide of azote.  Thus $3NO_3$, with excess of water, give rise to $HONO_5$ + water, and $2NO_2$. These changes depend on the proportions of water with which the compounds of azote and oxygen come into contact.

In the way the ordinary process of making sulphuric acid gas is carried on, it is almost always an adjunct to the manufacture of carbonate of soda.  Many of the manufacturers do not sell an ounce of sulphuric acid, but use it all to decompose muriate of soda, in the first step towards making the carbonate.  The process consists essentially

Fig. 21.
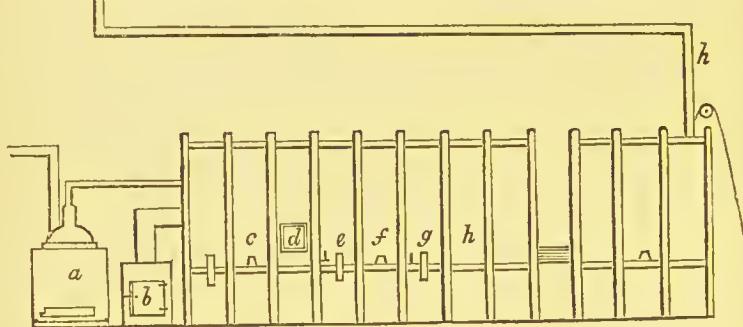


Fig. 21 represents the leaden chambers and apparatus used in the manufacture of sulphuric acid.  $a$ is a boiler for producing steam; $b$ a furnace for the production of the nitrous and sulphurous vapours. These furnaces have their connecting pipes with the lead chamber, as seen in the figure.  In the first leaden chamber, at $c$ and $f$, are contrivances to ascertain the depth of acid in the chamber, and there might be another at $h$; the floor of the chamber has as many ridges as may be desirable, formed by a transverse piece of lead, to collect the acid on the floor as the process goes on, of different strength, as at $c$ or $g$.  $d$ is a sort of door through which the chamber may be entered.  This chamber is connected with a smaller chamber, the exit pipe, from which $h$ generally enters into a condenser similar in principle to that used for muriatic acid.

in oxidising sulphurous acid by means of nitric acid.  For this purpose, sulphurous acid from burning sulphur or iron pyrites, nitric acid from nitrate of soda, acted on by sulphuric acid and steam, are introduced together into a leaden chamber, with water at the bottom; the steam is expelled from a common boiler; the sulphuric acid from burning sulphur enters along with the nitric acid, which is placed in a small iron basin, supported in the furnace where the sulphur is burned. The leaden chambers vary a little in construction; some are divided into partitions, having openings alternately at the top and bottom, so as to force the vapours to take a circuitous course, as in a still;—care is taken to admit air by valves.  The changes which take place are not

exactly understood; but the first effect must undoubtedly be, for the $SO_2$ to become $SO_3$, at the expense of the nitric acid, which will become $NO_4$; but this is readily resolved, as has been seen from the preceding observations, water being present, into nitric acid and nitrous acid, the latter into nitric acid and $NO_2$, which again, by contact with air, becomes $NO_4$. There is, therefore, a constant series of changes going on; and as sulphurous acid is readily absorbed by water, the probability is, that what nitric acid is absorbed by the water at the floor of the chamber, will meet with a considerable portion of sulphurous acid in the water, and form sulphuric acid there. Perhaps the best way of summing up the theory of the process is to say that it depends on the decomposition of nitric acid by sulphurous acid, and formation of sulphuric acid, while the peroxide of azote, $NO_4$, formed by the decomposition of the $NO_5$ is in a form which enables it, under the influence of water and air, to reproduce nitric acid, and probably in other forms, as $NO_3$ $NO_4$ yield oxygen to sulphurous acid. Only one
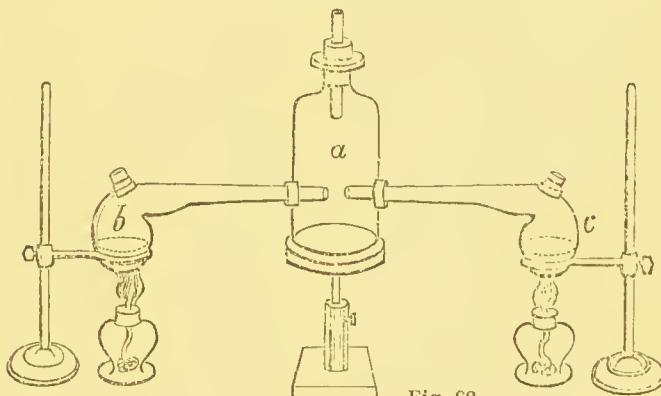


Fig. 22.

part of nitrate of soda is required to convert from 10 to 20 parts of sulphur into sulphuric acid.

The process is carried on until the water at the floor acquires a density of 1·35 to 1·50. The water is then run off, and used to make soda, in which case the former density is sufficient, or concentrated in platinum retorts until it acquires the sp. gr. of 1·848. This process may be imitated in an apparatus like that shown in Fig. 22. Two retorts, b c, are introduced into a jar, a, at the bottom of which there is water; the one is made to evolve peroxide of azote, and the other sulphurous acid; or the one may be made to evolve deutoxide of azote. A crystallised compound will form on the sides of the vessel, respecting which there are different views; some maintain it to be a compound of $NO_3$, sulphuric acid and water; others of $NO_5$, and the same substances. Be this as it may, it is decomposed by water, with formation of nitric acid, sulphuric acid, and binoxide of azote. This sulphuric acid contains 1 eq. of water, $HO,SO_3$. When the Nordhausen acid is subjected to distillation, and the receiver sur-

rounded with ice, there is collected a white solid, in long thin needles ; ; this is anhydrous sulphuric acid, which easily melts, boils at between 125° and 132°, has a sp. gr. of 1·97, and exhibits an extraordinary affinity for water, with which it unites with a hissing noise, and great evolution of heat.

Sulphuric acid of commerce will mix with water in any proportion ; but there are two mixtures which seem to possess more definite conditions than the rest—these are, the bihydrate $2HO,SO_3$ (this is the acid of sp. gr. 1·78), and the terhydrate $3HO,SO_3$, sp. gr. 1·632. The sulphuric acid of commerce freezes at 29°, and boils at 590°. But the bihydrate solidifies in prismatic crystals at 39°, and parts with 1 eq. $HO$ at a little above 400° ; while the terhydrate begins to part with its water at a little above 379°.

The ordinary test for sulphuric acid is to precipitate by means of it, or any soluble sulphate, a salt of baryta. Sulphuric acid is not the only salt which gives an insoluble salt with baryta ; but when the sulphate is collected, washed, and dried, and heated with charcoal, it is reduced to a sulphuret, which, treated with muriatic acid, evolves sulphuretted hydrogen, which gives a black stain to carbonate of lead test-paper put into the vessel whence the gas is evolved.

The sulphates or salts which this powerful acid forms with metallic oxides are in general readily formed by the addition of sulphuric acid to other salts of their bases. Sulphuric acid is considered as the most powerful of all acids. These salts, in their composition, resemble three at least of the hydrates of sulphuric acid. Thus the Nordhausen acid, $2HOSO_3$, is imitated by the bisulphate of potass, $2KO,SO_3$ ; and when the crystallised sulphate of magnesia is heated, it retains at a high temperature 1 eq. of $HO$, it is then closely analogous to the bihydrate, while the sulphates of 1 eq. of base, such as the anhydrous sulphate of soda, are analogous to the common acid of commerce. The sulphates are generally decomposed by ignition with carbon, with formation of sulphurets, carbonic acid and carbonic oxides being evolved and sulphurets formed ; in other instances the metals are reduced to the metallic form.[*]

Sulphuric acid has a most powerful action on organic substances, which in the first instance it chars ; it coagulates in the first place, and in excess dissolves albumen; hence it is a most powerful corrosive poison. Its best antidote is the use of chalk or magnesia with diluents.[*]

SULPHURETTED HYDROGEN, or HYDROSULPHURIC ACID, HS; Eq. 17; sp. gr. 1·912; combining vol. 1 ⬜.

This gas is not obtained by the direct union of its constituents. It is best prepared by the action of sulphuric acid and water on the sulphuret of iron, in the same kind of apparatus, and in the same way as in the preparation of hydrogen. Here the formula is very simple; $FeS + HO, SO_3 = FeO, SO_3 + HS$. Obtained in this way, the gas generally contains free hydrogen. It may be obtained in a purer form by heating the

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[*] Sulphuric acid of commerce often contains impurities, from most of which it may be freed by distillation. When prepared from iron pyrites, it almost always contains arsenic, sometimes in large quantities.

sulphuret of antimony with muriatic acid in a flask, and passing the gas through a wash bottle before collecting it or forming a solution of it. In this case, heat is required. Here the formula, sulphuret of antimony being a tersulphuret, is $3HCl + SbS_3 = 3HS + SbCl_3$; or chlorine in the terchloride is made to replace the sulphur of the tersulphuret, and the 3 eqs. of hydrochloric acid, which lose their 3 of chlorine to the antimony, give their hydrogen to the 3 of disengaged sulphur.

Hydrosulphuric acid is a colourless gas possessed of a very peculiar smell, as its solutions in water have a very peculiar taste. By strong heat it is partially decomposed. By a pressure of 17 atmospheres it is condensed into the liquid form. The gas burns with a blue flame, producing water and sulphurous acid. Chlorine, bromine, and iodine decompose it, taking the hydrogen and liberating sulphur. Nitric acid decomposes it by giving oxygen to its hydrogen and liberating sulphur. which excess of nitric acid will oxidate. Water at 60° absorbs $2\frac{1}{2}$ times its volume of this gas. Where sulphurets are in solution they become hydrosulphates, in the same manner as the chlorides; and when hydrosulphuric acid is passed into metallic solutions, and a sulphuret is thrown down, it is owing to the metallic oxide giving oxygen to the hydrogen of the hydrosulphuric acid, while the sulphur and metal combine and form a sulphuret, or, as it is now often called, a sulphide. With some metallic solutions, sulphuretted hydrogen alone can do this—with salts of lead, for instance; but with others, it is necessary to combine the hydrosulphuric acid with an alkali. The reaction is then favoured by double decomposition. For instance, hydrosulphuric acid will not decompose a solution of the sulphate of oxide of iron, but if ammonia be added, then the affinity of sulphuric acid for ammonia, leaves the oxide of iron at liberty to combine with the hydrosulphuric acid. This distinction is of great importance in the analysis of solutions containing metals, and enables two great classes of metals to be formed, viz. :— those whose solutions give precipitates with free hydrosulphuric acid, and those which require the hydrosulphate of ammonia.

Hydrosulphuric acid may be recognised by many of the characters given, chiefly by its action on metallic salts, and especially by the blackening of salts of lead.

It exercises a singularly deleterious influence both on animals and plants, acting like a narcotic poison on the former, and causing the leaves of the others to droop, and the plant to die, as if from a vital rather than a chemical effect.

Compounds of hydrogen and sulphur in other proportions, always with excess of sulphur, are obtained when solutions of alkalies or alkaline earths are boiled with excess of sulphur, and on decomposing one of these solutions, supposed to be a pentasulphuret, a light yellow liquid, called a pentasulphuret of hydrogen, separates.

## OTHER COMPOUNDS OF SULPHUR.

Sulphur combines with nitrogen, chlorine, bromine, iodine, &c. Perhaps its most important compound with the elementary non-metallic bodies is that with carbon, $CS_2$, eq. 38. This substance may be pre-

pared by passing the vapour of sulphur over carbon in a porcelain tube heated in a furnace, as in fig. 9; or iron pyrites, bisulphuret of iron, may be heated in an earthenware retort with ⅛th part of its weight of dry charcoal, in a furnace, the sulphur disengaged from the pyrites unites with the carbon at a high temperature. The bisulphuret of carbon is distilled, and then passed through a condensing tube into a bottle containing water, and kept cold by some of the ordinary means in use.

This substance is a colourless liquid which boils at $110^0$: its vaporisation in vacuo produces intense cold. It is extremely combustible, insoluble in water, but soluble in alcohol; dissolves sulphur, iodine, bromine, and phosphorus.

## 9. SELENIUM, Se.

Eq. 39. 28. This is an elementary body of a deep red colour, which, both in its physical and chemical properties, bears a close resemblance to sulphur, with which it is associated perhaps much more generally than is known: it has hitherto been found in very small quantities. Its known compounds closely resemble those of sulphur; it forms a selenious and selenic acid, selenites and seleniates, seleniuretted hydrogen, and seleniurets; and its compounds are isomorphous with those of sulphur.

## 10. PHOSPHORUS, P.

Eq. 32; sp. gr. of vapour 4327; combining measure, ½ vol.⬚. Phosphorus exists in large quantities in the bodies of animals, forming a large portion of their bones, and also of their fluids. It is also found in the vegetable and mineral kingdom. The usual mode of preparing phosphorus is as follows. After bones are burnt, and their animal matter thus destroyed, the residue is composed principally of phosphate of lime with some carbonate. This residue is treated with ⅔ds. of its weight of sulphuric acid, and 14 of water; the effect of this on the phosphate is as nearly as possible represented by the formula, $2 (CaO, PO_5) + SO_3 = CaO, SO_3 + CaO, 2PO_5$. Of course the carbonate of lime is decomposed, the sulphate formed, and carbonic acid driven off with effervescence, but the principal part of the process is the separation of one equivalent of sulphate of lime from two of phosphate, and the addition of the eq. of phosphoric acid driven off to the other eq. of phosphate, making an equivalent of the biphosphate $CaO, 2PO_5$; or at least, supposing the decomposition not to be so exact as this, an equivalent of phosphate of lime is kept in solution by the water containing excess of phosphoric acid. To effect the decomposition completely, the mass should be well stirred and digested for some hours on a sand bath. The liquid containing superphosphate of lime is then to be separated by filtration through a coarse cloth, concentrated to the thickness of a syrup, and well mixed with ¾ths of its weight of charcoal. The mass is then strongly heated and dried, and transferred, when cool, into a stoneware retort, to which a bent tube is attached, passing to the bottom of a vessel containing a little water, which should be kept cool. The excess of phosphoric acid in the

mixture is decomposed by the charcoal, carbonic oxide is given off, and the volatilised phosphorus drops into the water.

Phosphorus is a translucent solid of a yellowish, almost white colour, but exposed even under water to the action of light, it becomes of a red hue—hence, like sulphur, it is an example of allotropy.* Its sp. gr. is 1·77. It melts at 108°. It boils at 550°. It may be obtained by cooling from its solution in naphtha in regular rhomboidal dodecahedrons. It is insoluble in water, but slightly soluble in fixed and volatile oils, in ether, and other substances, one of which, the bisulphuret of carbon, has been named. Phosphorus and its compounds are isomorphous with arsenic and its compounds. It bears a close resemblance to this metal, even to the garlic smell they both possess.

Phosphorus oxidates slowly in the air, hence its use in eudiometry, as already mentioned. This slow combustion may terminate, especially in hot weather, or if the least friction be exerted, in rapid combustion. Some gases, chiefly hydrocarburets, prevent the slow combustion of phosphorus in air, it is supposed because they themselves have an affinity for oxygen.

The chief practical use to which phosphorus is applied, is in making lucifer matches. These have, in addition to sulphur, at the extremity, a mixture of phosphorus with some substance which readily yields its oxygen. The principal compounds with oxygen are the suboxide $P_2O$, hypophosphorus acid $PO$, phosphorous acid $PO_3$, phosphoric acid $PO_5$. With hydrogen it forms several compounds; it combines with many of the metals to form compound phosphurets (phosphides) of no very determinate character; and it also combines with many of the negative elementary bodies, as chlorine, bromine, iodine, sulphur, and selenium.

### Suboxide of Phosphorus, $P_2O$; Eq. 72.

This is easiest obtained by directing a stream of oxygen on phosphorus under water; phosphoric acid is formed, and oxide of phosphorus; as the former is soluble in water, the oxide of phosphorus remains, and may be washed and dried. It is a red powder, which, when heated, is converted into phosphoric acid and phosphorus. When the yellowish variety is exposed under water to the action of light, it becomes of a white colour externally, and under certain circumstances, while by a further exposure it is reddened; but by exposing phosphorus for a long time in an atmosphere free from oxygen and water, to a temperature approaching 500°, the fused phosphorus gradually becomes opaque and red. By digesting this in bisulphuret of carbon, the ordinary phosphorus attached to it is removed, and the amorphous variety remains. This variety differs from ordinary phosphorus in many respects; it is much less inflammable, is not luminous in the dark until near its burning point, requires a temperature of about 500° to inflame it, and, as has been ascertained by experiments on animals, totally differs in its physiological operations from ordinary phosphorus, producing none of those immediately formidable effects which ordinary phosphorus produces.

* The allotropic conditions of phosphorus are not well understood.

## Hypophosphorous Acid, PO, Eq. 40,

is prepared by boiling phosphorus in a solution of caustic baryta till all the phosphorus and the garlic smell disappear. There is formation of phosphoric acid, phosphuretted hydrogen, and hypophosphorous acid. Thus $6 (BaO,HO) + 4P = 3BaO,PO_5 + 3BaO,PO + 2PH_3$. The process may be considered analogous to that by which an alkaline hypochlorite is formed, except that, from the insolubility of the phosphate of baryta, it is sooner separated than is the chlorate; the liquid is filtered, the soluble hypophosphite separated from the insoluble phosphate, and decomposed by sulphuric acid, and as excess of this is required to be used to separate the baryta, it is got rid of by oxide of lead. The insoluble sulphate of lead is thus formed, and some free hypophosphite of lead is left in solution. To free the hypophosphorous acid from lead, sulphuretted hydrogen gas is passed through the solution, the sulphuret of lead is thrown down, the liquid is filtered, and freed from excess of sulphuretted hydrogen by evaporation. It can be concentrated to a thick syrup, but if heated beyond that, is decomposed, being resolved into phosphoric acid and phosphuretted hydrogen. It readily takes oxygen from other substances forming phosphoric acid, and combines with bases, forming crystallisable salts—hypophosphites.

## Phosphorous Acid, $PO_3$; Eq. 56.

This acid is obtained by the slow combustion of phosphorus. To effect this, phosphorus is burnt in a tube, to which the air is admitted by an orifice not larger than a pin hole; the tube is bent at an obtuse angle close to this orifice, and the phosphorus placed in the angle. It is heated then until it slowly burns; the phosphorous acid produced is volatilised, and condensed in the upper part of the tube. This acid, in a larger quantity of air, inflames, and is converted into phosphoric acid. It may also be obtained by throwing a few drops of water on the tercloride of phosphorus; the result then is easily explained by the formula $PCl_3 + 3HO = PO_3 + 3HCl$. It forms a hydrate containing 3HO. It forms phosphites, an indeterminate series of salts, inasmuch as they have always a tendency to form phosphates with water, with evolution of phosphuretted hydrogen. In all these reactions there is great analogy between the action of phosphorus on bases in contact with water, and the similar action of chlorine. In both cases, if the action be pushed to extremity, the tendency is to the formation of the higher acid, the compound with 5 eq. of oxygen; but the phosphorus has little real affinity for the metallic base; there is much more affinity between the base and chlorine, much more tendency to the formation of a chloride and chlorate, than to a phosphide and phosphate; for phosphuretted hydrogen, if it have acid properties, has these to much less extent than the hydrochloric acid; hence, instead of combining with the base, it is generally evolved.

## PHOSPHORIC ACID, $PO_5$; Eq. 72.

This acid may be produced by inflaming phosphorus in a capsule of platinum in the air upon a glass plate, and covering it, when inflamed, by a large vessel; the more air, of course the larger will be the quantity of phosphorus consumed. The phosphorus is converted into white flakes of phosphoric acid, which fall upon the plate. By an arrangement adapted to keep up a constant supply of air, a large amount of phosphorus may be burnt in this way, but it is not usually thus that a large amount of phosphoric acid is obtained.

One of the easiest modes is to oxidate the phosphorus by means of nitric acid. Nitric acid, diluted with an equal weight of water, is carefully heated in contact with phosphorus; the phosphorus is all dissolved, and on evaporating to dryness, phosphoric acid is obtained in combination with water. It may also be obtained by taking the solution of phosphate of lime in phosphoric acid, obtained in the process for preparing phosphorus, from the action of sulphuric acid on the phosphate, and decomposing this by carbonate of ammonia. This decomposes the phosphate of lime; carbonate of lime is thrown down, and phosphate of ammonia remains in solution; this is then evaporated, and heated in a platinum crucible, when the ammonia is driven off, and hydrated phosphoric acid remains.

Phosphoric acid has a remarkable character in its tendency to form compounds possessed of more distinct properties, with different equivalents of water, than other acids.

These compounds are first the monobasic or metaphosphoric acid. This acid is obtained by the action of nitric acid on phosphorus, as above stated. Its formula is $HO,PO_5$. The chief characteristic of this acid and its salts, where one eq. of base replaces the water, is, that they yield a white crystalline precipitate with nitrate of silver, and the acid itself coagulates albumen.

Pyrophosphoric acid, or deutobasic phosphoric acid, is obtained by evaporating the succeeding acid, the tribasic acid, in a platinum vessel, till the temperature rises to 415°. It may then be concentrated. A solution of this acid does not coagulate albumen, nor does it or its salts give a yellow precipitate with nitrate of silver like the succeeding acid, or a crystalline one like the preceding. This acid and its salts give a white flaky precipitate with nitrate of silver. This acid forms two classes of salts with metallic oxides, the acid pyrophosphates, which contain one eq. of the oxide, one of water, and one of acid—still 2 eqs. of base to one of acid; and compounds, where there are 2 eqs. of the oxide—still again two of base to one of acid. The formula of this acid is $2HOPO_5$.

Tribasic phosphoric acid, or $3HOPO_5$, is best prepared from the ordinary phosphate of soda, which is one of its salts. The composition of the ordinary phosphate of soda is $HO,2NaO,PO_5$, or 3 eqs. of base with one of acid. To obtain the terhydrate, this salt, purified by solution and recrystallisation, is dissolved in warm water, and decomposed by solution of sugar of lead, double decomposition takes place, phosphate of lead is thrown down, and acetate of soda remains in solution; the

tribasic phosphate of lead is then decomposed by sulphuretted hydrogen, and sulphuret of lead is precipitated, while phosphoric acid, as the terhydrate, remains in solution. The excess of sulphuretted hydrogen is expelled by heat. Solutions of this acid and its salts give a yellow precipitate with nitrate of silver.

To this subject attention will be again called under the head of soda.

### PHOSPHORUS AND HYDROGEN.

There are now three recognised compounds of these elements. $P_2H$ solid phosphuretted hydrogen, $PH_2$ liquid phosphuretted hydrogen, and $PH_3$, or gaseous phosphuretted hydrogen.

$P_2H$ is prepared when the phosphuret (or phosphide) of potassium, prepared by heating phosphorus and potassium under naphtha, is decomposed by water; a yellow powder is thrown down, which is the solid phosphuret of hydrogen.

$PH_2$ is formed when the gas derived from the action of water on phosphuret of calcium at a moderate heat, about from 140° to 150°, is passed into a bent tube, exposed to a freezing mixture. It is a colourless liquid, exceedingly inflammable; and it is supposed by some to give to phosphuretted hydrogen the power of inflaming spontaneously in the open air.

$PH_3$ PHOSPHURETTED HYDROGEN GAS; Eq. 35; sp. gr. 1·185; $\frac{1}{2}$ vol. of phosphorus, and 3 of hydrogen, condensed into 2 vols. ☐☐.

This gas may be obtained pure by heating crystallised phosphorous acid in a green glass retort. The hydrated phosphorous acid is resolved into phosphoric acid and phosphuretted hydrogen, according to the formula $4 (3HO,PO_3) = PH_3 + 3 (3HO,PO_5)$. So obtained, the gas is colourless, has a peculiar garlic smell, but it is not spontaneously inflammable. In fact, the inflammability which so distinguishes this gas is due to the combination of it with some of the liquid compound. In union with this, and possessing the property of spontaneous inflammability in air, phosphuretted hydrogen may be prepared by treating phosphorus with potassa, lime, or baryta, and water; various oxides of phosphorus are formed, and the hydrogen of the water unites with the phosphorus and escapes, the gas carrying with it some of the liquid compound, and taking fire as soon as it comes in contact with air. This is the chief property of phosphuretted hydrogen. It has acid properties, but to a very slight extent.

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## 11. CARBON, C.

Eq. 6, sp. gr. of vapour by theory 416; combining vol. 1 ☐; exists abundantly in nature in many forms, of which the purest is the diamond. Diamonds are formed either in regular octohedrons, or in a modification of this form, each triangular face of the regular octohedron being replaced by six triangular facets, giving to the crystal 48 facets. Diamonds can only be burnt at a high temperature, and are entirely resolved into carbonic acid gas.

Carbon occurs also in nature in the form of graphite or plumbago, black lead, and coal. Sometimes graphite occurs crystallised in plates— six-sided tables,—hence carbon is dimorphous; but generally it occurs in round masses. In this form it is generally associated with iron and manganese.

Coal is clearly of vegetable origin, produced by the combined action of heat and moisture on vegetable matter. Besides the remains of plants, coal contains a considerable quantity of inorganic matter, part of which, of course, would exist in the plant, but the greater portion is derived from the strata in which the coal is found, and portions of which have in the course of time been carried into the pores of the coal. Thus the ordinary salts found in water are all found in coal, alkaline and earthy sulphates, muriates, &c. &c. Sulphuret and sulphate of iron also are common constituents. Besides coal, the chief varieties of carbon are gas carbon, lamp black, wood charcoal, coke, and ivory black.

Gas carbon is the result of a slow deposition of coal at a high temperature; it is found lining the gas retorts. It has almost a metallic lustre, and strongly resembles black lead, sp. gr. 1·76. Lamp black is the soot of various oily compounds of carbon and hydrogen, in which the hydrogen, as the more combustible element, is present first, and from imperfect combustion a portion of the carbon is deposited. Wood charcoal.—Wood contains a large quantity of water, besides oleaginous compounds. In the formation of charcoal, the great end is to burn off these matters, drive off the water, and leave as much carbon as possible. Hence in the process air is very sparingly admitted. Charcoal has a remarkable power of condensing many gases, and of removing putrid effluvia, of preserving water from putrefaction on long voyages; and in general, remarkable antiseptic powers. These also are possessed by sulphur. Coke is the result of the exposure of coal to a similar treatment as that of wood in the manufacture of charcoal. Ivory black is the result of the calcination of bones in close vessels. One of the most important chemical facts in connection with charcoal is its power of withdrawing matter from solution, and decolourising solutions. Thus, if a solution of neutral sulphate of indigo be filtered through charcoal, the whole colouring matter is retained by the charcoal. This is a sort of chemical decomposition. It is thus used much in testing for poisons, to remove animal colours; and in the same way it has been shown to have the power of withdrawing organic poisons from solutions.

Carbon forms two compounds with oxygen.

CARBONIC OXIDE, CO; Eq. 14; sp. gr. 967·79; combining vol. 1 ☐ : and CARBONIC ACID, $CO_2$; Eq. 22; sp. gr. 1529; combining vol. also 1 ☐.

The former of these gases is best prepared by heating chalk with charcoal or iron, or both. When chalk is heated sufficiently, as in the process for making lime, carbonic acid is given off; and if this carbonic acid happens, when in the nascent state, to meet a substance having a strong affinity for oxygen, it divides its oxygen with it. Thus, if iron

be present, oxide of iron is formed at the expense of the carbonic acid; if carbon, then two equivalents of carbonic oxide are formed. Thus, $C + CO_2 = 2\,CO$. It is found most convenient to mix chalk with one-half its weight of charcoal and iron filings in equal parts, and heat them in an iron bottle. The gas may be collected over water. It should be passed through a wash bottle containing a little lime or caustic potash, to absorb any carbonic acid which may escape decomposition. This gas is hardly soluble in water, burns with a blue flame, and is converted into carbonic acid.

Carbonic acid is easily obtained by the action of an acid on a carbonate. The usual way is to act on chalk or marble with muriatic acid. The muriate of lime is formed, and carbonic acid liberated. The gas can be collected over water, in which it is soluble at the ordinary atmospheric pressure, to the extent of an equal volume.

When so obtained, carbonic acid is found to extinguish flame, and to be most deadly to animal life. From its great weight, it can be poured from a jar upon a taper like water, and extinguish it. The amount of carbonic acid which can be forced into water, or any other liquid, depends on the pressure to which it is subjected. It appears, at first sight, strange that it should be found easier to force carbonic acid into water than into alkaline solutions, as it might be supposed, in the latter, the attraction for the carbonic acid would enable a larger quantity to be with more facility forced in; but the fact appears to be, that the tendency of the presence of the salt in the water to drive off gas, overpowers this.

Carbonic acid is liquefied by a pressure of 30 atmospheres, at a temperature of 32°. When the liquefied carbonic acid prepared on the large scale, as in the apparatus of Thilorier, has the pressure of the gaseous atmosphere of carbonic acid relieved by the turning of a stop-cock, it resumes its gaseous condition with such rapidity, that by the heat absorbed for this purpose a portion of the acid is solidified. It is then a substance like snow, and melts at about 100°.

Carbonic acid gas is incombustible, and if poured, which its sp. gr. allows, on burning bodies, extinguishes their combustion. It reddens litmus feebly, and gives a precipitate with lime-water, which effervesces with the feeblest acids. A solution of carbonic acid in water has the power of dissolving many salts otherwise insoluble in water. In this way it is supposed that solution of carbonic acid derived from the atmosphere, may be the means of carrying many otherwise insoluble salts to the roots, and into the tissues of plants.

The gas appears to produce death in animals not only by its narcotic properties, but by producing a kind of strangulation, owing to spasmodic closure of the glottis when it is swallowed in a concentrated form. This is the way in which it operates when men are introduced into brewers' vats, where it has accumulated from the results of the process of fermentation; and in mines, after explosions arising from the sudden combustion of the carburets of hydrogen, by which water and carbonic acid are formed. In such cases, this gas is termed after-damp and choke-damp.

The best treatment in cases of poisoning by carbonic acid, is to let

the patient, as speedily as possible, have free access to air, and to throw cold water over the visage.

## COMPOUNDS OF CARBON AND HYDROGEN.

Carbon forms two most important compounds with hydrogen.

LIGHT CARBURETTED HYDROGEN, $C_2 H_4$; Eq. 16; sp. gr. 559·6; combining measure 2 vols. ▢▢

This gas is always formed when the compounds of carbon putrefy under water. It is best obtained by stirring the mud at the bottom of stagnant ponds, and, as the gas rises, inverting a jar full of water over the spot stirred. Obtained in this way, it contains a little $CO_2$, from which it may be separated by transferring the gas through lime water into another jar, and repeating the process twice or thrice. This gas forms the chief constituent of the air of coal-pits, and the inflammable gas of those mines, where, however, it is associated with nitrogen and carbonic acid, and in the German mines with its allied compound, the next gas to be described, the olefiant gas.

As this gas is formed by the union of 2 vols. of carbon vapour, sp. gr. 416, and 4 vols. of hydrogen, sp. gr. 69·26, and these fill 2 vols., the theoretical sp. gr. will be found by dividing the sp. gr. of $2C+4H$ by 2.

This gas may also be prepared by distilling a mixture of the acetate of soda, potassa, and quick-lime, at a rather high temperature.

A very important fact about this gas is its explosibility with air or oxygen. The limits of explosibility appear to be from 5—14 of air to one of the gas. Perhaps 1 $C_2 H_4$ to 10 of air is the most explosive mixture; if there be too much gas, or too little air, the explosive power is diminished. The products are $CO_2$, after-damp in mines, and HO.

The quantity of carbonic acid formed when this gas is detonated over mercury with oxygen exactly replaces the volume of the gas.

BICARBURETTED OR HEAVY CARBURETTED HYDROGEN—Olefiant gas, $C_4 H_4$; Eq. 28; sp. gr. 985·2; combining measure 2 vols. ▢▢

In this case 4 vols. of carbon vapour and 4 vols. of hydrogen are condensed into 2 vols., or as the combining measure is sometimes made a vol., although oftener 2, it is better to say that 2 vols. of each are condensed into 1, to form olefiant gas. Hence its sp. gr. is found by doubling the specific gravity of carbon and hydrogen, and adding them together.

It is prepared by heating together 1 measure of spirits of wine with 3 of sulphuric acid, till the liquid becomes black, and considerable effervescence takes place. A large retort should be used, and the heat carefully applied. The gas should be passed through large wash bottles, the first containing a little water, the second caustic potass in solution, and the third, which may be smaller than the others, oil of vitriol. The two first bottles should be immersed in cold water. After this, the gas should be passed through a U-shaped tube (see fig. 23) filled with pumice stone, soaked in oil of vitriol. It may then be collected over water rendered slightly alkaline by caustic potass. The

first bottle is meant to collect some alcohol and ether, which pass over undecomposed; the caustic potass is to absorb sulphurous acid and carbonic acid, which are also formed in this complicated process; the sulphuric acid is to get rid of any ether which may still remain; and at last the water is made slightly alkaline to finally clear the gas of any acid.
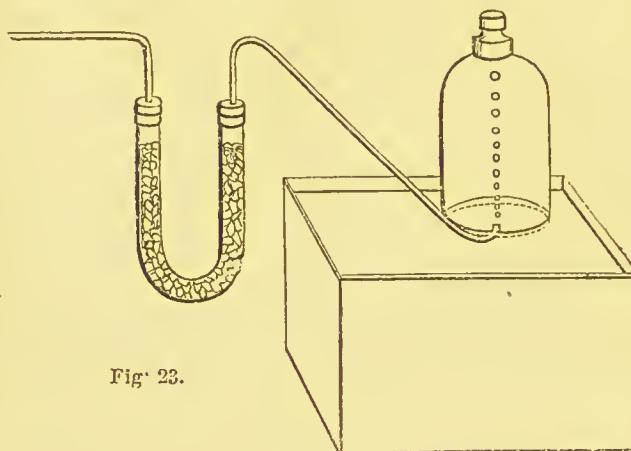


Fig. 23.

The decomposition which takes place may be best understood by considering, first, that alcohol may be regarded as a compound of olefiant gas and water. $C_4H_4,+2HO$, represents the composition of alcohol, although it is now regarded as the compound of an organic radical ethyl, whose formula is $C_4H_5$. On this view ether is said to be $C_4H_5,O$, or oxide of ethyl, and alcohol $C_4H_5,O,HO$, or hydrate of the oxide of ethyl. By the action, then, of sulphuric acid, the alcohol is resolved into olefiant gas and water, most likely by the affinity of sulphuric acid for the water; but other compounds are formed, a portion of the ethyl is decomposed, and carbon deposited. Hence the blackening and the evolution of carbonic and sulphurous acids by the action of carbon and other products on the oil of vitriol. In short, the process is not fully explained. According to the proportions in which sulphuric acid is mixed with alcohol, it depends whether the decomposition is arrested at the formation of ether, $C_4H_5O$; or whether this oxide of ethyl, already deprived of its water, which gave it the formula of alcohol, be further decomposed, and olefiant gas formed.

This gas has been condensed to the liquid form. Water absorbs one-eighth of its volume. It burns with a white flame, yielding the same products as its predecessor. It is entirely decomposed when passed through a red-hot porcelain tube. It requires three times its volume of oxygen to burn it completely. It then detonates much more powerfully than the light carburetted hydrogen. Hence the presence of this gas in the air of mines would be a matter of great im-

portance. It is found in the German coal mines, but not in those of this country.

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## THE SAFETY LAMP.

The various safety lamps which have been invented for mines are very interesting in their different details, but we have not space to describe them here. The reader should, however, understand the principle of the protective power of wire gauze, which is the basis of so many of them, and the sole protecting agent in that in common use —the Davy. It was known that flame would pass along tubes in the combined ratio of their width and length. The longer the tube, the wider it might be without the flame passing from one end to the other; and the narrower the tube, the shorter might be its length without damaging its protective power. The idea of wire gauze was an abstraction of this fact, as in wire gauze we have tubes of the shortest length and narrowest diameter. So, if air is admitted into lamps through tubes, the longer these tubes the wider they may be, without danger of an explosion in the interior of the lamp passing through and igniting any external inflammable mixture. The ordinary safety lamp, then, is merely a light surrounded with wire gauze, which allows the flame to be somewhat dimly visible, while the interposition of the gauze, under *ordinary circumstances*, is sufficient to prevent an explosion in the interior passing outwardly. See fig. 24.

OIL GAS.—This is a variety of olefiant gas, being twice as condensed. It is formed when the fixed oils are decomposed by heat, and yields a very brilliant light.*

COAL GAS.—This gas is a mixture of several compounds of carbon and hydrogen; and differs from the gas of mines in containing those products in addition to the light carburetted hydrogen. When coal is submitted to distillation at a high temperature, coal tar is obtained, a fluid containing much ammonia, and a gas containing light carburetted hydrogen, a large quantity of olefiant gas, and a great variety of compounds of carbon, sulphur, nitrogen, and hydrogen, as well as these three last elements themselves, and several other compounds in traceable proportions. The gas prepared on the large scale is first passed through tubes or pans, in which it deposits tar and a watery fluid: this part of the apparatus is termed the condenser. But the first of these tubes—a large tube—is termed

Fig. 24.

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* This and the preceding compounds of carbon and hydrogen may be separated in the following way:—Chlorine combines with olefiant gas and oil gas in the dark, forming an oily liquid, but will not combine with light carburetted hydrogen; when these gases, therefore, are mixed with chlorine in the dark, the two first are removed—the latter remains.
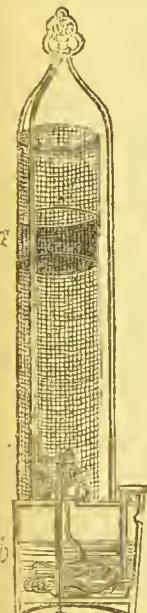
the *hydraulic main*. It is then allowed to enter an apparatus very similar in principle to the condensers of alkali works, described at p. 42, except that generally, instead of coke, the interior is formed of several shelves, over which water is allowed to run. Thus many of the gases are condensed. Sometimes, however, coke is used with the shelves. It is then passed through a washing apparatus containing milk of lime, or this mixed with sulphate of lead. Ammonia and sulphuretted hydrogen are the chief ingredients now absorbed. The salt of lead causes the formation of sulphate of ammonia and sulphuret of lead.

The process may be imitated on a small scale in an apparatus like the following:—The gas may be generated by heating coal in an earthenware retort in a furnace—the tube passing from this can be made to pass into a bottle like that in the figure, which will represent the condenser, and where tar and an ammoniacal liquor will condense. A tube from it can be passed through a Woolfe's apparatus filled with milk of lime; and after the gas has passed through this, it can be collected in a gasometer, or over water in a pneumatic trough. See fig. 25.
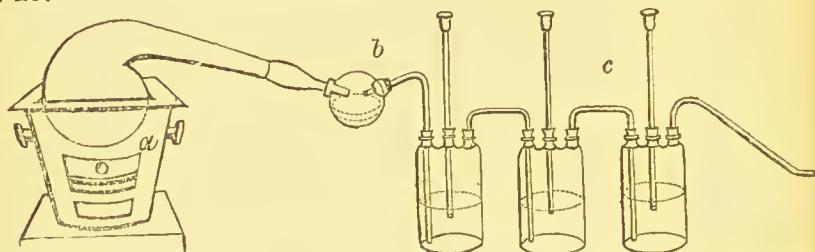


Fig. 25. The preparation of coal gas may be illustrated by heating some bituminous coal in an earthenware retort over a chauffer of charcoal, *a*; the gas and other products are first received in the bottle *b*, when two layers collect, the ammoniacal liquid above, and the tar below. It is then passed through the Woolfe's apparatus *c*, and then can be collected.

### Bi-Carburet of Azote—Cyanogen, Cy, $NC_2$; Eq. 26; sp. gr. 1819; combining vol. 1 $\square$ .*

This body is a gas, which is prepared by heating the cyanide of mercury in a small glass retort. The process is analogous to that for obtaining oxygen from the oxide of the same metal, the compound being resolved into cyanogen and metallic mercury. The gas must be collected over mercury. There is often found in the retort a black mass, isomeric with cyanogen—paracyanogen.

This gas explodes with twice its volume of oxygen, affording two volumes of carbonic acid and one volume of azote. Water at 60° absorbs 4·5 of its volume. By a pressure of 3·6 atmospheres it is liquefied. It burns with a beautiful purple flame. Its solution in water gradually undergoes decomposition. Alkaline solutions are acted upon by it in a mode analogous to the action of chlorine, a

* This compound deserves attention, as the first isolable compound radical which the student has yet arrived at.

cyanide, or hydrocyanate, and a cyanate being formed. Cyanogen is produced when azote is passed over fragments of charcoal saturated with potass, and heated, in a porcelain tube placed across a furnace, to a white heat. A cyanide of potassium is thus formed.

Cyanogen combines with the metals, which are either cyanides, MCy, or hydrocyanates of oxides, MO, CyH.

It forms three acids with oxygen CyO, cyanic acid, $Cy_2O_2$, fulminic acid, $Cy_3O_3$, cyanic acid, the important compound with hydrogen, hydrocyanic acid, and numerous other compounds. These rather belong to organic chemistry; but as some form important compounds with metals, which require to be discussed in inorganic chemistry, they shall be partly touched upon here.

CYANIDES AND HYDROCYANIC ACID.—The combinations of cyanogen and the metals form a beautiful series of salts, which, in their beautiful crystalline forms, resemble the finest salts in mineral chemistry. All the alkaline cyanides are soluble in water; the cyanide of mercury is also pretty soluble, but most of the others are insoluble, and are obtained by the action of an alkaline cyanide and a metallic salt, or by the action of hydrocyanic acid on the salt of a metal. This latter action, however, generally requires to be assisted by the presence of an alkali. Cyanogen generally combines with a metal in the same proportions as oxygen and chlorine. Thus, those metals which have an oxide, MO, have generally a cyanide MCy, and those which have an oxide $M_2O_3$ have generally a cyanide $M_2Cy_3$, or those which have a binoxide will have a cyanide $MCy_2$. Most cyanides are decomposed by other acids, in the same way as chloride of sodium by sulphuric acid, that is to say, with evolution of the hydracid, which acid is in this case the hydrocyanic acid. The cyanide of mercury is not acted on in this way. In general, the alkaline cyanides are little disposed to be decomposed by heat, while the metallic cyanides are easily so. All the cyanides treated by hydrochloric acid yield hydrocyanic acid, the decomposition not being difficult to be understood. Thus, $MCy + ClH = MCl + CyH.$.

In some cases cyanogen possesses the power of uniting with cyanides, so as to form what appears to be a new compound radical; thus a compound of the cyanide of iron with cyanogen is assumed, under the name of ferrocyanogen, to be a similar compound radical to cyanogen itself, and, when in solution, to be capable of a transformation which a cyanide would undergo, that is, to become a hydroferrocyanic acid in combination with an oxide. Thus the ferro*cyanide of potassium*, $K_2,FeCy_3 + 3HO = K_2O_2$ (or 2KO), $FeO,3(Cy_3H_3)$ (or $FeOCy_3H_3$); and it forms other similar compound radicals.

All the compounds of cyanogen with oxygen are isomeric, although very different in their properties, and they have a corresponding series in the compounds of cyanogen with chlorine. Thus there is a gaseous chloride of cyanogen, CyCl; a liquid, $Cy_2Cl_2$; a solid, $Cy_3Cl_3$. The compound radicals ferrocyanogen, just alluded to, and ferricyanogen, are also isomeric, the one being $Cy_3Fe$, and the other $Cy_6Fe_2$.

It may be seen from the remarks on these bodies how difficult it i s to draw the line exactly between organic and inorganic chemistry. If cyanogen could only be derived from the organic world, the case would have been different; but, as has been shewn, it can be formed by the direct union of its constituents in contact with potassa, under peculiar circumstances.

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## 12. BORON, B. ; Eq. 10·9.

Boron exists in nature in the form of boracic acid, the product of certain mineral springs or lagoons, chiefly in Tuscany, or in the form of borate of soda in similar lakes in Thibet, from which in the hot season it is obtained by spontaneous evaporation. When borate of soda in solution in water is decomposed by $SO_3$ or ClH, its boracic acid is separated, and, if the solution be a saturated one, is deposited in crystals. The boracic acid of commerce is obtained by concentrating the water of these lagoons.

Boron is obtained from boracic acid by heating it with potassium ; the potassium takes the oxygen, and after careful washing, the potassa is dissolved out, and boron remains as a dark green powder. Boron is not a substance of active affinities ; the chief use of its compound boracic acid—a very feeble acid—is to give to bodies a high degree of fusibility. Boracic acid, like an alkali, turns turmeric brown.

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## 13. SILICON, Si. ; Eq. 21·3,

May be prepared in the same way as boron, which it greatly resembles. It is principally interesting from its important compound silicic acid, found nearly pure in nature in the forms of rock crystal, quartz, flint sand, the various chalcedonies and agates ; and in the arts, along with soda, the basis of glass—perhaps the most important substance which human skill has ever invented. For where would be the sciences—nay, this very noble science of chemistry—without glass.

### SILICIC ACID, $SO_3$, Eq. 45·3, sp. gr. 2·66,

May be obtained artificially in several ways :—first, by heating together in a platinum crucible 1 part of fine sand and $2\frac{1}{2}$ parts of a mixture of the carbonates of potass and soda, in the proportion of their equivalents; the mass fuses and effervesces, owing to the escape of carbonic acid gas. The alkaline carbonates should be first put in, and the sand or any other siliceous material gradually added, and the addition continued until the effervescence is over. The mass having been allowed to cool, should then be dissolved in water acidulated with hydrochloric acid, which dissolves the whole. The liquor should then be filtered, and evaporated to dryness. The saline mass, when cold, is slightly washed

with strong muriatic acid, to dissolve out any alumina or iron. Then, after washing with hot water, the silica remains undissolved; or, secondly, it may be prepared by passing the terfluoride of silicon into water. This gas is formed when hydrofluoric acid comes in contact with silica. It may be regarded as $Si F_3$, and it is easily seen how $Si O_3 + 3 HF$ may result in $Si F_3 + 3 HO$ on the bringing of silicic acid and hydrofluoric acid in contact; but on this gas being passed into water, the $Si F_3$ is resolved with 3 eqs. HO into $Si O_3 + 3HF$; that is to say, silicic acid is deposited in the water into which the gas is passed, and hydrofluoric acid exists in solution. The fluosilicic acid, or terfluoride, is easily prepared by heating equal parts of fluor spar and sand in a glass retort along with six parts of concentrated sulphuric acid.

Silicic acid prepared by the former process is a white tasteless powder; is insoluble when dried, as stated, in almost all liquids. Sp. gr. 2·66. It is melted by the oxyhydrogen blow pipe. It crystallises in nature chiefly, as in rock crystal, as a six-sided prism terminated by a pyramid of the same number of sides. Silica may be obtained artificially crystallised, by precipitating a solution of silicate of copper in hydrochloric acid by sulphuretted hydrogen, which throws down the copper, and, by spontaneous evaporation in vacuo, the solution yields acicular crystals of silica.

The silicic acid prepared by the second process is gelatinous, soluble in water to some extent; the solution is tasteless, without acid reaction, and, on evaporation, gives a white powder, which is again soluble. Hence we have here two forms of silicic acid.

When a solution of an alkaline silicate is all at once decomposed by a large excess of acid, the silicic acid expelled remains in solution in the acid.

Silicic acid exists in solution in most mineral waters. In combination with bases it forms silicates; some of the most important of which are those with the alkalies.

The compounds with excess of alkali are soluble and caustic; but those with excess of silica are insoluble, and form the various kinds of ordinary glass. These compounds are not of a very determinate character.

*Glass.*—It is necessary in glass that there should be a union of different silicates, no single silicate possessing the requisite properties. Alkaline silicates always have more or less of the vitreous character. The silicates of earthy bases are not vitreous like the alkaline silicates, but slightly translucent, and more like porcelain than glass. The silicates of most of the metals are fusible, and more or less coloured.

In the manufacture of glass, the general object is to unite a certain degree of tenacity, and some colour, with transparency; and this is effected by a union of alkaline, earthy, and metallic silicates. The earthy silicates are opaque and crystalline; the latter defect, with the addition of too much colour, applies to most of the metallic silicates. The silicate of lead, which alone would be too fusible, imparts fusibility to other silicates of difficult fusibility.

To enter into the details of glass making would far exceed the

bounds of the preseut work ; " but the various kinds of glass may be distributed under the following heads :—

" 1. Silicate of potash aud oxide of lead.

" 2. Silieate of soda and lime, or silieate of potash, soda, and lime.

" 3. Silicate of potash and lime.

" 4. Silicate of soda, lime, alumina, aud oxide of iron.

" To the first class belong flint glass, crystal, aud strass; flint glass eontaius more oxide of lead than crystal, and strass more than flint glass. Common wiudow glass, English crown glass, aud plate glass, eonstitute the second elass in the above arrangement. Foreign crowu glass, aud the refraetory Bohemian glass, are the double silicate of potash and lime. The fourth class comprises the coarse green glass of whieh wine bottles are made."

It is very doubtful whether glass should be considered a definite chemical eompound, or a mixture ; but it appears that the nearer its constituents approach in their mixture to their equivalent proportious, in general the more perfect is the glass.

When glass in the molteu state is suddenly cooled, it is apt to assume a crystalline state ; and it is then easily broken, either by a blow, or sudden changes of temperature ; hence all glass for chemical purposes requires to be annealed—i. e., carefully eooled.

# PART III.

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## THE METALS AND THEIR COMPOUNDS.

THE properties most characteristic of the metals, are—1st, Their lustre, and power of reflecting light. 2nd, Their opacity; for it is only in the thinnest leaves that they possess translucency—never transparency. 3rd, Their weight for the most part, although potassium and sodium will float on water. 4th, Their generally high combining equivalents, although to this there are many exceptions. 5th, The property of malleability, which enables many of them to be beaten into thin plates or leaves; and the analogous property of *ductility,* which depends partly upon the cohesion of their particles enabling them to be drawn into fine wires.

Only one metal is fluid at ordinary temperatures, viz., mercury. Potassium and sodium melt below the temperature of boiling water. Most are very fixed; and platinum with its allied metals resist the strongest heat of a smith's forge, and can only be fused by the oxy-hydrogen blowpipe. The analogies between many of the metals and their compounds are very striking—between, for instance, barium and lead, and magnesium and zinc; and here, as among the non-metallic bodies, the physiological and medicinal relations follow precisely the chemical.

Metals have been formed into six groups :—1st, those which decompose water at 32°, or below it, with effervescence, *i. e.*, form oxides and liberate hydrogen; 2nd, those which, for this purpose, require a temperature approaching 212° or, at any rate, below a red heat; 3rd, which do not decompose water except at a red heat, or with the assistance of an acid; 4th, which decompose the vapour of water at a red heat, but which do not decompose water in the presence of the stronger acids; 5th, metals whose oxides are not decomposed by the influence of heat, and which only decompose water feebly, and at a high temperature; 6th, metals whose oxides are reduced by heat alone, and which do not decompose water under any circumstances.*

The general character of the metals is to form oxides with oxygen capable of uniting directly with acids. Of all the non-metallic bodies, hydrogen is the only one possessing this property. They also form, with the other non-metallic bodies, substances in which some element

———

* As the reader proceeds, he will perceive under what division each metal should be classed.

is substituted for oxygen,—as chlorides, bromides, iodides, sulphurets, &c. Finally, some metals form compounds of the same character with each other, as arseninrets; and metallic salts, as has been stated, combine with each other to form double salts, as acids with alkalies; the chloride of potassium, for instance, as an alkali, with the chloride of mercury as an acid.

There is every reason to believe that the progress of science will resolve some of the metals into more simple forms; and that something like the dreams of the alchemists may at a future period be realised. The different metals will be treated of under the following heads:—

1st, Metallic bases of the alkalies; 2nd, metallic bases of the alkaline earths; 3rd, metallic bases of the proper earths; 4th, metallic bases whose *oxides* are isomorphous with magnesia; 5th, metals whose compounds have isomorphous relations with the same family; 6th, metals isomorphous with phosphorus; 7th, metals not included in the preceding groups, whose oxides are not reduced by heat alone; 8th, metals whose oxides are reduced to the metallic state by heat; 9th, metals found in native platinum.

Sect. 1. METALLIC BASES OF THE ALKALIES. These are three—Potassium, Sodium, and Lithium; and to these may be added the hypothetical metal Ammonium.

## 14. POTASSIUM OR KALIUM, K.

Eq. 39. Potassium was first obtained by the decomposition of potassa by galvanism; it was then procured by the decomposition of the same alkali by means of iron at a white heat, oxide of iron being obtained, and potassium, which is a volatile metal, distilled over. It is now always procured by the decomposing action of carbon. For this purpose, a quantity of cream of tartar, or bitartrate of potass, is ignited in a crucible. The tartaric acid, which is a vegetable acid, containing carbon, oxygen, and hydrogen, is decomposed, and resolved into carbon and water, and carbonic acid. The latter combines with the potass, so that, when the ignition is over, there remains in the crucible a mixture of carbon and carbonate of potass. This is put into a retort, or bottle with a short iron tube, say a portion of a gun barrel attached to it, and heated in a wind furnace by a most intense heat; the product is distilled into a copper receiver of a peculiar construction, and which contains Persian naphtha, a liquid containing no oxygen, and is surrounded with ice. The products of the distillation are chiefly potassium and carbonic oxide, formed by the decomposition of the carbonate of potass by the carbon, which first reduces the carbonic acid of the carbonate to the form of carbonic oxide, and then reduces the potassa itself by taking its oxygen; but there is also formed and found in the receiver a black mass very rich in potassium, partly a carburet, carbonic acid, and some oxalate and carbonate of potass. The potassium and the black mass are redistilled in an iron bottle, and the product received into naphtha. Potassium is then obtained pure.

Potassium melts at 150°, but softens at a lower temperature. It is

volatile at a low red heat. Its sp. gr. at 60° is 0·865. Exposed to the air, it gradually oxidates. As has been mentioned, it takes fire in water or on ice, leaving its protoxide potassa behind. Inflamed, it burns in oxygen, and the result is the teroxide $KO_3$, which, on being put into water, loses its excess of oxygen with effervescence, and becomes KO, or potassa.* Potassium has as yet no other uses than to remove oxygen in chemical analysis, and in obtaining boron and silicon, and the bases of the alkalies and earths. It is isomorphous with ammonium, sodium, and silver.

### POTASSA, KO ; Eq. 47.

Anhydrous potassa can be obtained by heating the hydrate KO, HO, with an equivalent of potassium in an atmosphere free of air. When it is added to an equivalent of water, much heat is disengaged.

### HYDRATE OF POTASS—*Caustic Potass*, KO, HO ; Eq. 56.

This compound is obtained from the carbonate of potass. Equal parts of this salt and quick-lime are used. The latter is first slaked with water, when it falls into a powder consisting of hydrate of lime. The two are then boiled together, with four or five times their weight of water, in an iron pan. The lime has more affinity for carbonic acid than the potass, probably owing to its property of forming an insoluble carbonate.† When a little of the clear liquid taken from the pan does not effervesce on the addition of an acid, all the carbonic acid has been removed from the potass, the pan is then covered with a lid, and allowed to cool. The clear portion is then run off by a syphon into an iron or silver evaporating dish, and rapidly evaporated. The remaining portion may be filtered through a coarse cloth, the top of the funnel being covered with a plate, and the fluid received into a bottle, to allow as little access of air as possible. The mass, when all its water is expelled by evaporation, except the eq. of basic water, fuses, and may be cooled and broken into pieces, or, when fluid, run into moulds, when it forms the sticks of caustic potass used in medicine. Obtained in this way, it contains a little of the carbonate ; this is removed by solution in alcohol, which dissolves the hydrate and leaves the carbonate. The alcoholic solution can then be evaporated, as the watery one had been before.

Pure potass is a white mass, sp. gr. 1·7, fusible at a red heat. It rapidly destroys the animal tissues. It melts at a red heat, and volatilises at a high temperature. It dissolves rapidly in water, with much evolution of heat. On account of its great affinity for water, hydrate of potass is used to dry substances in the vacuum of the air-pump. For this purpose, a porcelain dish like that represented in fig 26 is used. It is divided into cells by partitions, which approach, but do not meet in

* This action of water on $KO_3$ bears an analogy to the action of ClH on $BaO_2$, in the preparation of oxygenated water.

† The action is stopped if too little water is used—*i. e.*, if the power of separation of the soluble potass, and insoluble carbonate of lime, by the water, be diminished.

the centre. The cells are filled with the drying substance. The dish containing the substance to be dried is supported as shown in the figure. On exhausting the air in the receiver, water rises from the substance to be dried, but it is absorbed by the potassa or other substance having a



great affinity for water; more vapour rises, and is absorbed in the same way. Exposed to air, it absorbs water and carbonic acid. The alkaline reactions of potass are well marked. Its compounds with acids are well defined. With oil it forms soaps. From its affinity for silicic acid, it cannot be long boiled in glass or porcelain vessels without some action on them.
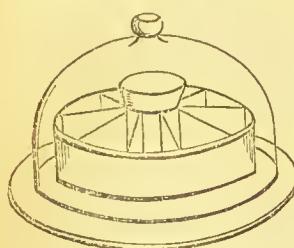
Fig. 26.

Free potass or soda in solutions of their carbonates may be discovered by means of nitrate of silver. This salt gives the brown oxide with the alkalies, but a white carbonate with their carbonates. Salts of potass are thus distinguished from those of soda and other salts; 1st, in any solution containing 1 per cent. of a salt of potass, tartaric acid in excess, and dissolved in a little water, throws down the insoluble white crystalline bitartrate; 2nd, bichloride of platinum throws down yellow octohedral crystals, which are a double chloride of platinum and potass; 3rd, most of the salts give a violet colour to flame.

The principal compounds of potassium with other elementary non-metallic bodies than oxygen, are the chloride, bromide, iodide, and sulphurets; of these the iodide and the sulphurets are of most importance.

### Iodide of Potassium, $KI$; Eq. 165·36.

This important salt is easily prepared by decomposing the iodide of iron by means of carbonate of potass. For this purpose a solution of iodide of iron is first formed, which may readily be done by mixing 2 parts of iodine and 1 of iron filings in a flask, with 10 or 12 parts of water. The iron is in considerable excess, in order that the protoxide of iron may be formed. A little heat completes the combination. The solution is then filtered and decomposed by solution of carbonate of potass, as long as a precipitate is formed. This precipitate is carbonate of iron, and the decomposition is represented by the formula $FeI + KO,CO_2 + HO = FeO,CO_2 + KI$; or, if we consider the iodide a hydriodate, by the formula $FeO, IH + KO, CO_2 = FeO, CO_2 + KO, IH$. This salt may also be obtained by adding iodine to a solution of potassa, evaporating to dryness and igniting; the iodide of potassium and iodate of potass are formed, and by the process of ignition the iodate is deprived of its oxygen just as the chlorate of the same base is in the process for preparing oxygen, and all the mass is converted into iodide. The bromide may be procured by precisely similar processes. The iodide may be obtained from its solution in water in cubes or rectangular prisms. Its solution possesses the power of dissolving a large quantity of iodine.

Sulphurets or Sulphides of Potassium.—Of these there are several. The protosulphuret is formed when hydrogen is passed over sulphate of potassa at a red heat. It may also be prepared by fusing sulphur with excess of potassa; for $3 (KO, HO) + S_4 = 2KS + KO, S_2O_2 + 3HO$. It may be obtained pure by saturating a solution of potassa with hydrosulphuric acid, and afterwards adding as much potassa as had been before employed. In the first instance, the hydrosulphate of sulphuret of potassium is formed; and in the second, the hydrosulphuric acid is transformed into a sulphuret of potassium, or, in solution, a hydrosulphate of potassa, KO, SH, being $= KS + HO$. This solution may be evaporated to dryness, when it will yield a white crystalline mass.

Sulphuret of potassium deliquesces; the solution has a bitter taste, and yields sulphuretted hydrogen when treated with acids. The solution gradually absorbs oxygen, and has been used for this purpose in eudiometry. The bisulphuret $KS_2$, the tersulphuret $KS_3$, the quadrosulphuret $KS_4$, and the pentasulphuret $KS_5$, may all be obtained by fusing the protosulphuret with the proper or equivalent quantity of sulphur.

*Hepar sulphuris*, or liver of sulphur, so called from its colour, is obtained by fusing sulphur and carbonate of potass. Two parts of the latter are used to one of the former. The compound is a mixture of the tersulphuret of potassium with hyposulphite of potass, carbonic acid being disengaged during the process. This substance is conveniently used for preparing extemporary sulphur baths.

## Cyanide of Potassium, KCy; Eq. 65.

This salt may be prepared by the addition of hydrocyanic acid to a solution of potass in alcohol; a portion of the cyanide is formed as a white crystalline precipitate, which should be well washed with alcohol, and dried; or it may be prepared from ferrocyanide of potassium (prussiate of potass). This salt is a compound of the compound radical ferrocyanogen and potassium. Its formula is $K_2FeCy_3 + 3HO$. The salt is dried, powdered, and 8 parts of it, 1 of charcoal and 3 of carbonate of potass are ignited in an iron vessel. The iron is partly oxidised, and partly combined with carbon; the residual mass is powdered and washed with cold water. A solution of the cyanide is obtained, which is to be quickly evaporated to dryness, and fused. This salt crystallises in cubes. Exposed to the air, it is partly decomposed by the carbonic acid of the air, with evolution of hydrocyanic acid, partly it absorbs oxygen, and passes into the state of cyanate.

*The prussiate of potass* itself is formed by fusing carbonate of potass at a red heat, in an iron pot, with refuse animal matters; afterwards, by lixiviation and crystallisation, those splendid yellow crystals of the prussiate are obtained. The crystals are in the form of quadrangular tables, with truncated angles and edges. They contain 3 eq. of water, which are driven off at 212°, are very soluble in cold and hot water, but insoluble in alcohol. Ferrocyanogen is a compound radical, $FeCy_3$, and is bibasic—*i. e.*, combines, as in this salt, with 2 eq. of base. Its eq. is $184 + 27$ (HO). (The process for

preparing cyanide of potassium, as described at p. 67, has been tried on the large scale with the view of making prussiate of potass and Prussian blue from it; but, it is believed, without success, in a commercial point of view. The process, however, is highly interesting, as an instance of the formation of a substance generally considered as an organic compound, by the direct union of its constituents.)

### The Ferricyanide of Potassium, or *Red Prussiate of Potass*, $3K,Fe_2 Cy_6$; Eq. 329.

This salt is obtained by passing chlorine gas through a solution of the preceding salt, till it ceases to give a precipitate of Prussian blue with a persalt of iron. The nature of the change will be understood when we see that $2 (K_2FeCy_3) + Cl = K_3Fe_2Cy_6 + KCl$ ; in other words, the chlorine removes the potassium, and forms chloride of potassium with 1 out of 4 elements of potassium when we double the eq. of yellow prussiate, and the atoms arrange themselves differently. It may be separated from the solution of chloride by crystallisation. It forms right rhombic prisms of a fine red colour. The crystals are anhydrous, and of about the same solubility as the yellow prussiate. This salt gives a blue precipitate with protosalts, as its predecessor does with persalts of iron.

This salt is supposed to contain another compound radical, *Ferricyanogen*, which is tribasic.

### Sulphocyanide of Potassium.

Another compound of a compound radical. It is obtained by heating the ferrocyanide with an equal weight of sulphur in a crucible of iron. A mixture of sulphocyanides of potassium and iron is formed. Both are dissolved in water, and the iron precipitated by carbonate of soda (which throws down carbonate of iron); the solution is then evaporated, and gives crystals of sulphocyanide of potassium. These may be freed from any remaining carbonate by dissolving them in alcohol. The crystals are white striated prisms. This salt gives a blood-red colour to solutions of the persalts of iron.

### SALTS OF THE OXIDE OF POTASSIUM.

*Carbonate of Potass*, $KO,CO_2$; Eq. 69.

This salt is chiefly obtained from the ashes of plants. These, in the form of pearlash, are mixed with about 20 per cent. of foreign salts, chiefly sulphates. The pearlash is dissolved in an equal weight of water, which dissolves the carbonate and leaves other salts undissolved. From the solution, evaporated to dryness, a nearly pure carbonate is derived.

Carbonate of potass may be prepared purer by igniting cream of tartar, bitartrate of potass, as in the process for preparing potassium, or mixed with nitre. Carbonate of potass remains mixed with carbon, from which it may be separated by solution.

This salt is very deliquescent, and soluble in less than its bulk of water. It is alkaline.

*Bicarbonate of Potass*, $HO,CO_2+KO,CO_2$, Eq. 100, is prepared by passing a stream of carbonic acid through a saturated solution of the neutral carbonate, and evaporating this by a gentle heat. This salt crystallises in eight-sided prisms. It is soluble in 4 parts of water at 60°, and more so in boiling water. The solution is less alkaline than that of the carbonate. It readily yields its excess of carbonic acid when heated.

The *Acetate of Potass* is readily formed by dissolving the carbonate in acetic acid. It is a very deliquescent salt. Several other compounds of potassa with vegetable acids are formed in the same way.

*Nitrate of Potass*, $KO,NO_5$; Eq. 101.

This important salt is formed when animal substances are decomposed in the air in contact with an alkali. Nitric acid is produced by the disposition to combine with a base, causing, as it were, the nitrogen of the animal matter to become oxidised. It occurs native in India, and is obtained by washing out some of the soils. In Europe it has been manufactured by exposing decomposing animal substances in contact with lime to the air. The nitrate of lime is first formed; this is lixiviated, and wood ashes added to the solution; carbonate of lime is thrown down, and nitrate of potass remains in the liquid.

This salt crystallises in long six-sided prisms, which are striated. Its crystals contain no water. It is soluble in less than 4 parts of water at 60°. The chief use of this salt is in making gunpowder. Nitrate of soda is generally now substituted for it, as a source of nitric acid. The best English gunpowder contains 12·5 of sulphur, and the same of charcoal, with 75 of nitre. By theory, the best formula for gunpowder would be 11·9 of sulphur, 13·5 of charcoal, and 74·6 of nitre. This is about 1 eq. of nitrate of potass to 3 of carbon and 1 of sulphur. Now 3 eq. $C+KO,NO_5+S=3CO_2+N+KS$, that is to say, 3 of carbonic acid, 1 of azote, and 1 of sulphuret of potassium.

*Sulphates of Potass.* — The sulphate is prepared by dropping sulphuric acid into a concentrated solution of potassa. It precipitates, being one of the least soluble potass salts. The bisulphate, which is much more soluble, is obtained when nitric acid is made by the action of 2 eq. $SO_3$ on $KO,NO_5$. From this the sulphate may be obtained by neutralising it with the carbonate.

*Chlorate of Potass*, $KO,ClO_5$, Eq. 122·5, is formed when chlorine is passed through a strong solution of carbonate of potass. The water is decomposed, its oxygen going to one portion of the chlorine, and its hydrogen to another—thus chloric acid and muriatic acid are formed; but for every equivalent of the former there must be five of the latter. Muriate and chlorate of potass are the results. The chlorine is passed through till the liquor ceases to absorb any gas; and as the chlorate is much more insoluble than the muriate, it is gradually deposited in tabular crystals, which must be purified by a second crystallisation. This salt is anhydrous. 100 parts of water at 59° only dissolve 6 of it. It detonates with inflammable substances much more powerfully than nitre.

## 15. SODIUM, $N_A$.

Eq. 23.　This metal can be prepared by a method similar to that for obtaining potassium, viz., by calcining a mass of the acetate of soda, whereby a mixture of charcoal and carbonate of soda is formed, and heating this as in the mode of preparing potassium.

Sodium is very like potassium externally; like it, it is soft. It melts at 194°. It absorbs oxygen from the air, but does not burn like potassium, when thrown on water. It rapidly, however, decomposes the water absorbing oxygen, while hydrogen escapes with effervescence. When heated to redness, it takes fire and burns with a yellow flame, very different from the violet hue of the flame of potassium. Sodium in its compounds occurs extensively in the mineral kingdom, in the form of common salt especially, and forms part of the composition of vegetables and animals. When sodium is burnt in oxygen it forms a peroxide, not $NaO_3$, analogous to the peroxide of potassium, but $NaO_2$.

### Soda, NaO ; Eq. 31.

Soda is obtained from its carbonate by means of lime, in the same way as potassa is prepared. It is soluble in all proportions in water and alcohol.

Soda is distinguished from other bases, and especially from potassa, by the following properties :—1st, all its salts are soluble in water ; 2nd, like the metal itself when it burns, they give a rich yellow tint to flame, with the exception of the muriate ; 3rd, they form a soluble salt, which crystallises in prisms with sulphuric acid.

### Chloride of Sodium (Common Salt), NaCl; Eq. 58·5.

This salt may be formed at once by putting sodium into chlorine ; it takes fire, and the salt is the result; or it may be procured by dissolving the carbonate in hydrochloric acid ; but, in practice, it is always obtained either from mineral sources, as rock salt—for it exists in many parts of the world literally in mountains—from salt springs, or from sea-water. It is obtained from sea-water by evaporating to a certain extent, and then allowing the solution to crystallise. The mother liquid or bittern is then used principally for the magnesian salts which it contains. It crystallises from its solution in cubes, and sometimes from bittern in octohedrons. The crystals contain no water. Its solubility, according to some, is the same in hot and cold water ; but this is denied by others. Its solubility varies from 60° to 212°, so that at the former temperature water will dissolve rather less than a third, and at the latter, less than a fourth. When a solution is exposed to a very low temperature, as near 5°, the salt crystallises in hexagonal tables.

This salt is slightly deliquescent, is very soluble in alcohol, fuses at a red heat, and is volatile at a higher temperature. Its sp. gr. is 2·557. Its important uses in domestic economy are well known. Besides these, it has extensive uses in manufactures, in preparing muriatic acid ; and, as we shall soon see, in the making of carbonate of soda. It has the power when brought, at a high temperature, in contact with

clay in which oxide of iron exists, of decomposing the oxide of iron. Sodium combines with the oxygen of the oxide, and the chlorine with the iron, forming the chloride of iron, which is volatilised. When chloride of sodium and silica are heated together in the presence of watery vapour, muriatic acid is driven off, and silicate of soda formed. It is upon these two decompositions that the glazing of pottery depends. A quantity of salt is cast into a kiln, volatilised by the heat, and this vapour condensing on the pottery in the kiln causes the vitrification of the outer surface with escape of muriatic acid and chloride of iron.

The bromide and iodide very much resemble the chloride. They are both milder in their physiological action than the corresponding salts of potassium.

SULPHURETS OF SODIUM.—Very similar to the corresponding compounds of potassium.

### SALTS OF THE OXIDE OF SODIUM.

*Carbonate of Soda*, $NaO,CO_2+10HO$; Eq. $53+90$.

This salt occurs in nature principally in the *trona* lakes in the pashalick of Tripoli. Here, at certain seasons, some lakes, when at the lowest, leave by evaporation on their shores vast masses of the carbonate of soda, which is carried into the interior of Africa, and there used as a substitute for salt. It is extensively manufactured in the present day by a process which is about to be described, and which constitutes one of the greatest triumphs of the application of chemistry to the arts. Notwithstanding the crude materials employed in this process, the results, the oblique prismatic crystals which are obtained, and which we see so commonly sold, are nearly pure, containing hardly one per cent. of impurity. These crystals contain 11 eqs. of water, and are composed therefore of 21·81 soda, 15·43 carbonic acid, and 62·76 water. Their sp. gr. is 1·623. They effloresce, *i. e*, lose water, when exposed to the air. They require rather less than 5 times their weight of water at 60° to dissolve them; but are soluble in an equal weight of boiling water.

When they effloresce they lose five eqs. of water, and become $NaO,CO_2+5HO$. Carbonate of soda has alkaline properties. When heated, it first melts in its water of crystallisation; and when this is driven off, the residual salt itself melts at a higher temperature. When steam is passed over the carbonate of soda at a red heat, the carbonic acid is driven off by the steam, and the hydrate of soda $NaO,HO$ is formed. The dry carbonate of soda contains 58·58 soda, and 41·42 carbonic acid.

### MANUFACTURE OF CARBONATE OF SODA, OR ALKALI MANUFACTURE.

At one time this salt, so important in the arts, and especially in the making of glass and soap, was obtained from barilla and kelp (see iodine), and accordingly a very large income was derived by many proprietors of estates, in Scotland and Ireland especially, by the burning

of the sea-weed into kelp. When the process about to be described
was discovered, the first result was a serious loss to these proprietors;
and the manufacture of kelp almost ceased. Now, however, thanks
to the discovery of iodine, and the uses of the potash salts obtained
from kelp in the manufacture of alum, the process of making kelp has
again come into pretty extensive use,—a striking proof how wrong it is
to ask the *cui bono* of scientific discoveries, since here we have the
discovery of iodine, repairing to some extent the loss which many had
sustained by the new mode of manufacturing soda.

The first step in this process consists in decomposing the muriate
of soda with sulphuric acid. For this purpose, what is called a rever-
berating furnace is used—so called because the air is made to pass over
the whole of the materials, and to impinge upon the back of the fur-
nace, so as to reverberate, as it were, upon them. See Fig. 27. The
first furnace is called the decomposing furnace. Some of the furnaces
are simple, others double. In the first of these, sulphuric acid, gene-
rally of sp. gr. 1601, is let in from the roof on an equal weight of
muriate of soda already heated. The charge of muriate of soda is
generally 600 pounds. Of course great ebullition occurs, and escape
of muriatic acid gas. The residual sulphate is either then heated as



Fig 27.
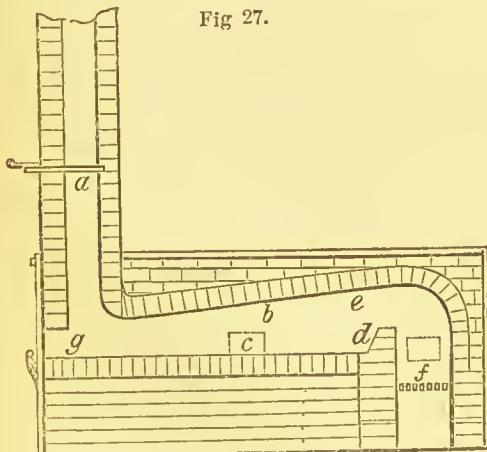
Fig. 27 represents a per-
pendicular section of a rever-
berating furnace;—*f* is the
grating and fireplace; from *d*
to *g* is the floor of the fur-
nace, where the materials to
be roasted are placed; *c* is an
opening for the introduction
of materials; *g* another open-
ing for their occasional re-
moval; *a* is a damper; from
*e* and *b* towards the chimney
is the reverberating roof.

long as fumes are given off in the single furnace, or raked over into the
other compartment if the furnace be double. At any rate it is dried
and removed. When there are two compartments, one is called the
decomposing bed, and the other the roasting bed. The sulphate of
soda, so obtained, is known under the name of " salt cake." The sul-
phate of soda being obtained, the next step is to calcine it with chalk
or fragments of limestone, and small coal. This is done in a furnace
similar to the one described, but called the " black ash furnace." From
10 to 13 parts of the salt cake are mixed with from 12 to 14 of lime-
stone, and from 5 to 9 of coal, the proportions differing in different
manufactories. Some hundredweights or a ton of these materials,
according to the size of the furnace, are introduced. The furnace is

divided into two parts, one called the preparatory bed, where the materials are thoroughly heated, and the other called the fluxing bed, where they are exposed to a still more intense heat. They are raked from the one to the other. In the fluxing bed, jets of burning sulphuretted hydrogen, carburetted hydrogen, and carbonic oxide, are given out, termed "candles" by the workmen, and the mass is kept constantly stirred until the jets of flame nearly disappear; it is then raked out into cast-iron moulds, where it solidifies, and these black masses are called black ash, or British barilla. It is also called ball-soda, and the process the balling process.

This process consists essentially in the decomposition of sulphate of soda by carbon and hydrogen existing in the coal, and its reduction to the state of a sulphuret, which by the presence of the carbonate of lime is decomposed, the result being carbonate of soda and sulphuret of calcium. Black ash should contain from 25 to 30 per cent. of alkali. The insoluble matters are carbonaceous matters,—carbonate of lime, and a sulphuret of calcium with lime;—the soluble constituents, carbonate of soda, sulphuret of sodium, caustic soda, undecomposed sulphate of soda, and common salt.

The next step in the process has for its object to separate the soluble constituents of black ash from the carbonaceous and other insoluble matters present. In order to effect this, the black ash is broken into pieces, and put into iron tanks, where it is lixiviated with water. In the course of a few hours the lixivium is drawn out; this washing or lixiviation is several times repeated, and the solutions are all evaporated to dryness, and then calcined in a reverberatory furnace, termed the white ash furnace. The result is called "soda ash," which contains a sufficient quantity of soda for many purposes, as in most glass manufactures: it is sometimes rendered purer by a fresh calcination in a reverberatory furnace, which removes a portion of sulphur, and causes some caustic soda to combine with more carbonic acid. Sometimes the second calcination is performed with saw-dust and charcoal mixed with the soda ash. The ash dissolved in water yields, by crystallisation, the common carbonate of soda nearly pure; and the mother liquid, evaporated to dryness, gives a residue which still contains enough soda to be useful for many purposes.

The principal objects, then, in the soda process are to convert the sulphate of soda into a sulphuret, and to act upon this by carbonaceous materials, so as to drive off, with the aid of heat, all the sulphuret, in the form of sulphurous acid, sulphuretted hydrogen, or to combine it with lime, in the form of sulphuret of calcium. Thus, in the balling process, the lime acts a double part: it both furnishes carbonic acid, and a base for the sulphur to combine with. The residue, after the various lixiviations, constitutes the tank waste, and is composed of sulphuret of calcium, along with many other substances, as might be expected from the nature of the materials used.

## ALKALIMETRY.*

It is an object of importance to ascertain how much acid is required to neutralise a certain portion (say 100 grains) of a salt of soda. For this purpose a vessel is used, called an alkalimeter; see fig. 28. This is graduated by means of a
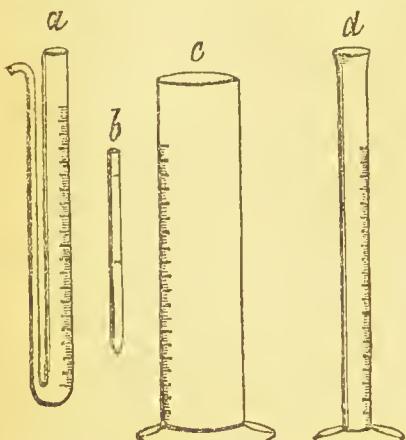


pipette, *b*, which has marked on it divisions corresponding each to a bulk of mercury, equal to the space occupied by 50 grains of water. This will be equal to 678·40 grains of mercury. There may be two of these divisions. By pouring the mercury carefully from this pipette into a long jar, *d*, the jar may be graduated into divisions corresponding to 50 grains of water each, and these can be divided by measures into spaces each corresponding to 5 grains of water. The jar should be able to hold at least 1000 grains of water: the divisions should be numbered 5, 10, 15, and so on to 100.

Fig. 28.

Three-fourths of an ounce of bicarbonate of soda are then heated strongly for an hour, so as to obtain pure carbonate of soda. Of this 170·6 grains, containing 100 grains of basic soda, are taken. Four ounces avoirdupois of sulphuric acid are mixed with 20 ounces of water. The alkalimeter is filled to the top of the divisions, which proceed from above downward, with a solution of the carbonate of soda, to which the acid is added by degrees until the alkaline reaction is destroyed, and the amount of acid required to do this noted, as it is better to have the acid of such a strength that 100 measures of it may saturate exactly 100 grains of soda. For this purpose a jar *c* is taken, such as is represented in fig. 28, which is graduated so into 100 parts, as that each $\frac{1}{100}$th may contain 100 grains of water. This jar is graduated from below upwards. Whatever amount of dilute acid was necessary to neutralise 100 grains of soda, is put into this, and sufficient water is poured in to make it up to 100 measures. The remaining portion of the acid which had not been tested as to its neutralising power is diluted in the vessel *c* in the same proportion as the specimen examined, and the whole acid liquor kept in a bottle for use. 100 measures of it would neutralise 100 of soda. Twenty-two measures of it neutralise 100 grains of the ordinary crystals of the carbonate, and 58·5—100 of the perfectly dry carbonate. The application of it to the examination of any soda salt in solution is easily made. If 30 measures of the acid be required to neutralise 100 grains of the salt, then it con-

* See Graham's Chemistry.

tains only 30 per cent. of soda. In few cases is any more manipulation necessary. $a$ represents another form of the alkalimeter.

*Bicarbonate of Soda*, $HO,CO_2 + NaO,CO_2$, may be prepared by passing a stream of carbonic acid through a solution of carbonate of soda, and carefully evaporating, or by, as is always done on the large scale, exposing crystals of carbonate of soda to a current of carbonic acid gas. The water of crystallisation is expelled, and a salt remains of the above formula. Its properties are well-known.

*Sulphate of Soda*, $NaO,SO_3 + 10HO$, is left after the process for making hydrochloric acid. It crystallises in long prisms which effloresce in air, and ultimately lose all their water. The crystals are slightly soluble in very cold water. Water at 91° dissolves at most 3·22 parts, and in heating above this point to 212°, crystals in the form of rhombic octohedrons which are anhydrous are deposited.

The *Bisulphate* is formed by adding one eq. of $SO_3$ to one eq. of the neutral sulphate in solution; and it may be crystallised from the solution.

*Hyposulphite of Soda*, $NaO,S_2O_2$. This salt, which is now much used in the photographic process, is first procured by forming the sulphite of soda, by passing a stream of purified sulphurous acid into a solution of carbonate of soda till the latter is neutralised; and then for some days digesting, with the aid of heat, the solution of the sulphite with sulphur. From the solution filtered and carefully evaporated, crystals of the hyposulphite are obtained.

*Nitrate of Soda*, $NaO,NO_5$, occurs native principally in America. It crystallises in the rhombohedral form. It is brought to this country in large quantities to be used for disengaging nitric acid in the manufacture of soda.

## PHOSPHATES OF SODA.

1st. *Common Tribasic Phosphate of Soda.* — $NaO,HO,PO_5 + 24HO$.

Calcined bones are to be treated with sulphuric acid as in the process for making phosphorus. An acid phosphate of lime is formed, which is decomposed by carbonate of soda. The solution evaporated, yields prismatic crystals. By adding soda to this salt in solution, an eq. of soda may be made to take the place of the eq. of basic water, forming $3NaO,PO_5 + 24HO$. This salt is called the subphosphate; and by an addition of phosphoric acid to the common phosphate, a salt of the composition $NaO,2HO,PO_5 + 2HO$, called superphosphate, may be formed. This is also called the acid phosphate. Nitrate of silver in solution gives with the common phosphate a yellow precipitate containing three of oxide of silver to one of base,—the nitric acid being found in the liquid. The subphosphate gives a similar precipitate, and so does the acid phosphate;—all these phosphates being tribasic, whether their base be alkali or water. The common phosphate is soluble in four parts of water at 60°. The solution is alkaline.

*Pyrophosphate of Soda.*—Eq. $2NaO,PO_5 + 10HO$. When crystals

of common phosphate of soda are heated, they melt in their water of crystallisation, and in cooling form a glass which has the composition which follows, from the expulsion of all the water of the common phosphate, viz., $2NaO,PO_5$. When this glass is dissolved in water, it retains its bibasic property, and crystallises in the form indicated by its formula. This salt has an alkaline reaction, and gives a white precipitate with solution of nitrate of silver, $2AgO,PO_5$, pyrophosphate of silver. Here the solution is neutral, for $2NaO,PO_5 + 2 (AgO, NO_5) = 2AgO,PO_5 + 2(NaO, NO_5)$. When the acid tribasic phosphate is heated to nearly 400°, it loses 1 eq. of its water, and becomes the acid pyrophosphate $NaO,HO,PO_5$, which, however, still gives rise with the nitrate of silver to the pyrophosphate of silver, the salt of soda being still bibasic, although one of its eq. of base is water. As the formula of the decomposition must be then $NaO, HO, PO_5 + 2(AgO, NO_5) = 2AgO, PO_5 + NaO, NO_5 + NO_5,HO$, the liquid left behind is acid.

*Metaphosphate of Soda.*— Eq. $NaO, PO_5$. This salt is obtained by strongly heating the acid triphosphate. Of course, all the water being driven off, a salt of the above formula will remain. The fused mass, cooled slowly, forms a crystalline glass; allowed to cool quickly, it forms a fusible deliquescent glass. Its solution gives, with nitrate of silver, the monobasic metaphosphate, a white precipitate.

The constitution of these phosphates has been differently represented.

*Biborate of Soda, Borax,* $NaO,2BO_3 + 10HO$, is found in the water of lakes in Thibet; and is now manufactured from the boracic acid springs of Tuscany. It is made by simply adding crude boracic acid to solution of carbonate of soda, boiling the two together, and after allowing the impurities to subside, crystallising the salts. This salt is much used in blowpipe experiments to fuse ores, earths, &c.

*Phosphate of Soda and Ammonia,* $NaO,NH_4,8HO,HO,PO_5$, is prepared by mixing solutions of seven parts of the phosphate of soda and one of muriate of ammonia hot. On the solutions cooling, this salt crystallises. Its chief use is in blowpipe experiments.

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## 16. LITHIUM, Li.

Eq. 6·5. A very rare metal exists in some rare minerals, as spodumene, lepidolite, petalite. It bears great resemblance to potassium and sodium; but is a connecting link between them and the alkaline earths.

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## 17. AMMONIUM, Am.

$NH_4$. Eq. 17. The ground on which this substance has been supposed to exist has been already alluded to.

Hydrogen and nitrogen are supposed to form three compounds :— AMIDOGEN, $NH_2$; AMMONIA, $NH_2 + H$ or $NH_3$; and AMMONIUM, $NH_4$.

*Amidogen*, Ad, has been proved by analysis to exist in the white precipitate whose symbol is expressed by $HgCl,HgAd$.

When several compounds of ammonia are heated, they also furnish substances in which the azote and hydrogen most probably exist in the form of amide of a base. Thus, when oxalate of ammonia is heated, it is decomposed, and a white sublimate is obtained (oxamide), which is regarded as a compound of carbonic oxide and amidogen, $NH_2,C_2O_2$. The formula of oxalate of ammonia is $NH_4O,C_2O_3$. Thus, taking away 2 eqs. of water, which are driven off by heat, we get *oxamide*. This substance differs from the oxalate in being very insoluble.

AMMONIA (the gas),—$NH_3$, sp. gr. 591 ; combining measure, 2 vols. ☐ ; is formed when organic matters are decomposed by heat, or in their putrefaction. The gas is generally prepared either by heating the solution in water, or by the decomposition of muriate of ammonia by slaked lime. The muriate is mixed with an equal weight of slaked lime, and heated in a retort or flask, with a bent tube connected with it. Chloride of calcium is left in the retort, and ammoniacal gas disengaged, or $NH_4Cl + CaO = NH_3 + CaCl + HO$. The gas can either be passed into water, or collected over mercury.* Ammoniacal gas is colourless, and has a well-known odour. It burns in air in contact with flame. It can be condensed into the liquid form by a pressure of 6·5 atmospheres at 60°. One volume of azote and three of hydrogen, in forming it, are condensed into two volumes. It may be resolved, at a red heat, into its elements, when passed through a porcelain tube containing copper wire. Mixed with an equal vol. of $NO$, it may be exploded by electricity being resolved into water and azote. Water absorbs no less than 700 times its volume of ammonia. The most concentrated solution has a sp. gr. of 0·875. Ammoniacal salts can easily be made to give off their ammonia by heating them with lime or potassa, and the ammonia given off may be recognised by its power of forming white fumes when a glass rod dipped in muriatic acid is brought near them, or by their action when conducted into a solution of sulphate of copper. A precipitate is first formed, which, if the ammonia be in sufficient quantity, is redissolved, and a fine blue colour produced. The solution of sulphate of copper should not be strong if the ammonia is likely to be in small quantity. Ammonia may be distinguished from the fixed alkalies by the circumstance, that its action upon turmeric testpaper and vegetable blues is but temporary, owing to the volatility of the alkali.

Solution of ammonia in water may be regarded as that of a hydrate of the oxide of ammonium of unstable character, $H_4O + HO = NH_3 + 2HO$.

Ammonia forms compounds with *anhydrous* acids and other bodies, which are not the same with the compounds of oxide of ammonium.

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* When it is passed into water, an apparatus similar to that used in preparing muriatic acid may be employed, except that very little water should be put into the central receiver.

Thus 4 vols. of ammonia and 2 of carbonic acid form a light volatile powder, which is supposed to exist in the ordinary carbonate, and to be the source of its strong ammoniacal smell. It forms similar compounds with other acids, and several compounds, more or less definite, with salts, some of which will come under consideration.

CHLORIDE OF AMMONIUM (Sal-ammoniac), $NH_4$; $AmCl$; Eq. 53;

is obtained when ammoniacal vapours and fumes of muriatic acid meet, and when ammonia is passed into solution of muriatic acid. It was formerly brought from Egypt where camel's dung is used as fuel. By heating this, muriate of ammonia was sublimed. It is now almost always obtained from the ammoniacal liquids which are procured during the manufacture of gas, or of animal charcoal, from bones. These liquids contain carbonate of ammonia and sulphuret of ammonium. Both are decomposed by adding hydrochloric acid, and the muriate of ammonia is crystallised from the solution. It is then heated to destroy organic impurities, re-dissolved, purified by boiling with animal charcoal, and, finally, after crystallisation, sublimed.* As thus prepared, it forms a crystalline cake exceedingly tough, and difficult to powder. Its sp. gr. is 1·450. It crystallises in cubes, octohedrons, or six-sided pyramids, which are gathered together like a mass of plumage. It is soluble in a third of its weight of water at 60°, and great cold is produced. At 212° it is soluble in its own weight of it.

Similar compounds with bromine and iodine exist.

SULPHURET OF AMMONIUM, $NH_4$,S, or $AmS$; eq. 34.

It is formed in solution when sulphuretted hydrogen gas is passed through a solution of ammonia, and then a fresh equivalent of ammonia added. Excess of hydrosulphuric acid at first forms a bihydro-sulphate of the oxide of ammonium, or hydrosulphate of the sulphuret, $NH_4S + SH$, from which the ammonia takes the excess of hydrosulphuric acid, thus —$NH_3,SH = NH_4,S$. It may be obtained crystallised by the distillation of chloride of ammonium and sulphuret of potassium into a receiver surrounded by a freezing mixture. The solution of the sulphuret of ammonium rapidly loses ammonia when exposed to the air, acquires colour, and passes into the state of bisulphuret. The sulphuret is alkaline, and acts the part of a base to some of the electro-negative sulphurets. Under the name of hydrosulphate of ammonia, hydrosulphate of the oxide of ammonium ($NH_4$,S + HO, being equal to $NH_4$,O + SH), it is much used as a re-agent.

Several other sulphurets may be formed by distilling the various sulphurets of potassium with chloride of ammonium.

### SALTS OF AMMONIUM.

CARBONATES OF AMMONIUM.—*Sesquicarbonate of Ammonia*, 2

* It may be obtained by converting the carbonate of ammonia in the liquid from bones into sulphate by sulphate of iron, and decomposing the sulphate formed by chloride of sodium, separating the muriate of ammonia and sulphate of soda by crystallisation, the former crystallising first; and by other modes.

$NH_4O,3CO_2$. The carbonate of ammonia, generally known under this name, is of a varied composition, but in general approaches nearest to the above formula. It is prepared by heating muriate of ammonia with twice its weight of chalk, and condensing the sublimate.* The decomposition is not easily formularised, inasmuch as the sublimate is not always of the same composition, but there is interchange of the carbonic acid of the chalk and muriatic acid or chlorine of the ammoniacal salt with their respective bases, and carbonate of ammonia and muriate of lime are formed. The salt sublimed seems to contain the neutral carbonate of ammonia described already; for, on treating it with water when, as already said, the $NH_3$ would become $NH_4O$, the result is the resolution of the sesquicarbonate into $NH_4O,CO_2$, and the bicarbonate, a compound of one eq. of oxide of ammonium with 2 of



Fig. 29.
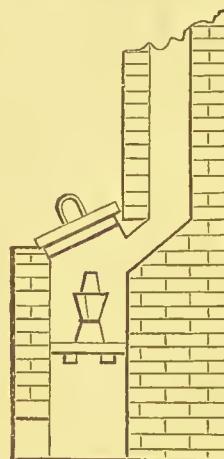


Fig. 30.

carbonic acid and one of water. When a solution of the sesquicarbonate in hot water cools, crystals of the bicarbonate are formed. The same salt is formed by passing a stream of carbonic acid through a saturated solution of the sesquicarbonate, and deposited in crystals. The sesquicarbonate is soluble in 3 parts of water.

Numerous compounds of ammonia and carbonic acid have been described.

*Sulphate of Oxide of Ammonium*, $NH_4O,SO_3+HO$, may be prepared in the laboratory by the action of sulphuric acid on sesquicarbonate of ammonia; on the large scale, prepared by the action of $SO_3$ on the ammoniacal liquors of gas works, and subsequent crystallisation. Its crystals are six-sided prisms, containing 2 eqs. of water, one of which they readily lose when heated.

*Nitrate of Oxide of Ammonium*, $NH_4O,NO_5$, is prepared by acting on the sesquioxide with nitric acid. The solution is easily rendered

* This process is best conducted on the small scale in an alembic. (See fig. 29.)

neutral.   On evaporation, crystals of six-sided prisms are formed, iso-
morphous with nitrate of potass.   This salt is soluble in 2 parts of
cold water.  It deflagrates like nitre.  Many of its properties have been
already described.

Sect. 2.   METALLIC BASES OF THE ALKALINE EARTHS, compre-
hending Barium, Strontium, Calcium, and Magnesium.

### 18. BARIUM, Ba.

Eq. 68·64.   This metal is prepared by passing the vapour of potas-
sium over baryta, at a red heat, in an iron tube.   The barium is reduced
in the tube, and is amalgamated with mercury, which is afterwards dis-
tilled off from the barium in a glass retort, at a temperature below a red
heat.   Barium is like the metallic bases of the alkalies in external ap-
pearance ; but it sinks in sulphuric acid, and, when put into water,
sinks in it, disengaging hydrogen as it descends, and forming a solution
of baryta.

#### OXIDE OF BARIUM—Baryta, BaO ; Eq. 76·64.

Is best obtained by calcining the nitrate of baryta.   It is a greyish
white powder of sp. gr. 4.   By passing oxygen over it heated to redness
in a porcelain tube, it is converted into the binoxide $BaO_2$, which is used
in preparing oxygenated water. It slakes and falls to powder when water
is thrown on it, and the result is a hydrate, BaO,HO.   In order to pre-
pare the hydrate of baryta as a reagent, the sulphate is reduced to
powder, and mixed with $\frac{1}{3}$rd powder of charcoal, and $\frac{1}{4}$th of resin; it is
then put into a Cornish crucible, which is heated by a strong fire to
bright redness for at least an hour.   A furnace like that represented in
fig. 30 is proper for such a process.   The sulphate is decomposed, pre-
cisely as is the sulphate of soda in the alkali manufacture, by the car-
bon, and sulphuret of barium is formed.   The crucible is then allowed
to cool, and the mass is treated with boiling water, which dissolves out
the sulphuret of barium.   To this solution, brought to the boiling
point, black oxide of copper is added, till a drop of solution of acetate
of lead is not blackened by a drop of the former solution added to it,
and till, in fact, a white precipitate is formed.   This solution should
be kept from the air for use, or it may be rapidly evaporated; and if
sufficiently concentrated, crystals of a hydrate with 10 eq. water may
be obtained.   In this process, oxide of barium, subsulphuret of copper,
and hyposulphite of baryta are formed, the former only being soluble.
The formula of the decomposition is $6BaS + 8CuO = 5BaO + BaO$,
$S_2O_2$ (hyposulphite of baryta) $+ 4Cu_2S$.
   *Hydrate of baryta* (BaO,HO) is soluble in 3 parts of water at 212°,
and 20 at 60°. The reactions of baryta are more like those of potassa
than of lime.   When chlorine is passed through it, it is resolved like
potassa into a chloride of barium and a chlorate.

### CHLORIDE OF BARIUM, $BaCl+2HO$; Eq. $104\cdot14+18$.

May be prepared either by dissolving carbonate of baryta, which is found native, in muriatic acid, or where this is not to be had, by decomposing the solution of the sulphuret, prepared as described in the preceding process with ClH, until the liquid is neutral; sulphuretted hydrogen is evolved, and a solution of the muriate remains, which can be evaporated and crystallised. It crystallises in flat four-sided tables, which contain 2 eq. of water, as represented in the formula. It is a valuable reagent for sulphuric acid, which it throws down in the form of insoluble sulphate.

The bromide and iodide of barium may be prepared in the same way as the analogous salts of potassa. The sulphuret has no other use than what has been described.

*Carbonate of Baryta*, $BaO,CO_2$, Eq. $98\cdot64$, is easily prepared by decomposing the muriate by an alkaline carbonate.

*The Sulphate and Nitrate of Baryta* are readily obtained by the action of their respective acids on salts of baryta. The former is insoluble except in strong sulphuric acid. The salts of baryta give a white precipitate with phosphate of soda, soluble in nitric and muriatic acids; a crystalline precipitate with hydrofluosilicic acid, a white precipitate with oxalate of ammonia, and are precipitated by solution of sulphate of lime; they are distinguished from salts of lead by the action of sulphuretted hydrogen, which blackens the latter. They give a yellow colour to flame.

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Note : The salts of baryta closely resemble the salts of lead, with which they are isomorphous, in most of their properties. It is worthy of remark, that if we halve the eq. of barium, and add the half to a whole equivalent, we get $102\cdot96$, very near the equivalent of lead, $103\cdot54$.

The physiological properties of the salts of baryta are very similar to those of the salts of lead. The carbonates of both are powerful poisons, while their sulphates are inert. Can this be owing to the acids of the gastric juice being capable of acting upon the carbonates, forming from them the soluble salts of baryta and lead, as clorides of barium and lead, &c., while they are without action on the sulphates ?

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### 19. STRONTIUM, Sr.

Eq. $43\cdot84$. Strontium closely resembles barium, and is prepared in the same way. Its oxide and salts also closely resemble those of barium, with which they are isomorphous. They are distinguished from the latter by the action of hydrofluosilicic acid, which may also be employed to separate them; this acid precipitating baryta, but not strontia. The salts of strontia, especially the nitrate, give a red colour to flame, and are employed to produce the red lights at theatres.

## 20.   CALCIUM, Ca.

Eq. 20.   This metal may be obtained in the same way as barium, and is analogous to it, but much lighter.

### Oxide of Calcium (Lime), CaO; Eq. 28.

Lime is obtained either by heating ordinary limestone, carbonate of lime, or the purer marbles, to redness in a lime-kiln or open fire. By this process the carbonic air is expelled.   The lime remains in porous masses.   For use in the laboratory, Carrara marble may be heated to full redness in a covered crucible.   The sp. gr. of lime is 2·3, or, according to some, 3.   Water thrown upon lime is first absorbed, and then combines chemically with the lime, forming a true hydrate, containing 1 eq. of water, which falls into powder.   Previous to this the lime is called quick-lime, or unslaked; in the state of hydrate it is said to be *slaked*.   Great heat is given out in this process, so that meat may be cooked by it.   The temperature may rise considerably above 500°.

Lime in its solubility in water is an exception to the general rule, for it is more soluble in cold than in hot water.   At 60° it is soluble in 778 parts of water, but requires 1270 for its solution at 212°.   When the solution is evaporated in vacuo, hexahedral crystals of the hydrate are formed.   Lime-water is easily prepared by agitating for some time distilled water with considerable excess of lime in a stoppered bottle, and allowing the solution to remain over a quantity of undissolved lime.   A rather tall bottle should be used for the purpose.   It is an excellent test for carbonic acid, causing a precipitate of carbonate of lime in fluids containing either that acid free, or an alkaline bicarbonate. A little lime-water exposed to the air is rapidly covered by a pellicle of the carbonate.   Lime-water does not give a precipitate with sulphuric acid, although its soluble salts, except when very dilute, do so.   The reason of this is, that the sulphate of lime is not so insoluble as the sulphates of baryta and strontia.   The uses of lime in agriculture, and in the formation of cements, are well known.

### Chloride of Calcium, CaCl; Eq. 55·50.

Is easily obtained by the action of muriatic acid on carbonate of lime. The solution is generally evaporated to dryness, and the residue instantly broken in pieces and put into jars, kept closely corked, and secured from access of air.   But the concentrated solution yields crystals, striated four-sided prisms, which contain 6 eq. of water.   When these crystals are dried in vacuo over sulphuric acid, they yield a hydrate in the form of a crystalline powder, which contains 2 eq. of water.   Anhydrous boiling alcohol dissolves chloride of calcium, and on cooling in a freezing mixture, yields crystals in which 2 equivalents of alcohol are substituted for 2 of water in the hydrate.

Chloride of calcium, from its great affinity for water, is much used in drying substances, and especially in organic analysis.

Bromides, iodides, phosphurets, and sulphurets of calcium, may be formed.

## FLUORIDE OF CALCIUM, CaF; Eq. 38·70.

Is found native, as in the beautiful coloured cubic and octohedral crystals known as Derbyshire spar. It exists also in sea water, and in bones, especially in the enamel of the teeth. It is formed when a soluble fluoride is mixed with a solution of neutral salt of lime, and then is thrown down as a gelatinous mass.

### SALTS OF LIME.

*Carbonate of Lime*, $CaO,Co_2$, Eq. 50, occurs abundantly in nature, either in amorphous masses of limestone rocks or chalk, or in crystals, as in the numerous forms of calcareous spar. The primitive crystals are the rhomboid and six-sided prism. Carbonate of lime may be obtained in the form of a crystalline hydrate. Carbonate of lime is so insoluble, that it requires nearly 9000 times its weight of boiling water to dissolve it, and it is still less soluble in cold water. Its solution is alkaline. Carbonate of lime is soluble in excess of carbonic acid, and it is in that way that it is held to such an extent in solution in natural water, which, when exposed to the air, allows the carbonic acid to escape, which is immediately followed by deposition of the carbonate. It is in this way that stalactites are formed. When lime-water is added to a water containing carbonate of lime so held in solution, by removing the excess of carbonic acid in the form of carbonate of lime, it causes the precipitation of the carbonate originally present. Thus $CaO,CO_2 + CO_2 + CaO = 2 (CaO,CO_2)$. Thus the whole carbonate is rendered insoluble. The hardness of river or spring water is often due to the carbonate of lime present. (See Mineral Waters.)

*Sulphate of Lime*, $CaO,So_3 + 2HO$, Eq. $68+18$, occurs extensively in nature, both crystallised and amorphous. It is soluble in about 400 parts of water, at all temperatures. Heated in small lumps, so as to be made anhydrous, and then pulverised, it forms plaster of Paris, which powerfully absorbs water, and thus forms the well-known cement or stucco, which also is useful in the laboratory. In agriculture it has extensive uses.

### PHOSPHATES OF LIME.

There are two phosphates of lime besides the acid phosphate used in the preparation of phosphorus.

*Triphosphate of Lime* is prepared by adding chloride of calcium to triphosphate of soda. Thus $(3NaO,PO_5)$ added to $3CaCl = (3CaO,PO_5) + 3NaCl$. It falls as a gelatinous precipitate.

Ordinary *Phosphate of Lime* is prepared by the addition of common phosphate of soda $(2NaO,HO,PO_5)$ to chloride of calcium. Thus, adding to the phosphate of soda $2CaCl$, we get $(2CaO,HO PO_5) + 2NaCl$. This is precipitated like the foregoing. The phosphate of lime in bones is the former of these two salts.

*Hypochlorite of Lime*—Bleaching powder. The substance ordinarily called bleaching powder is a compound of the chloride of calcium and hypochlorite of lime with water. It is a white and somewhat moist powder, and its formula is $CaCl + CaO,ClO$ ; but it is generally mixed with carbonate of lime, and perhaps with other salts little known, compounds of the various oxides which chlorine forms, and lime. When chlorine acts upon an alkaline base, the first tendency is to the formation of a chloride and hypochlorite, thus—$2KO + 2Cl = KCl + KO,ClO$. This takes place in weak solutions of the alkalies, as has been explained; but these solutions rapidly undergo decomposition, and when strong alkaline solutions are used, the tendency appears to be for the hypochlorous acid to contribute to the formation of more stable compounds, and the decomposition of the hypochlorite to go on more and more to the formation of a chloride and chlorate, by the withdrawal of oxygen from one equivalent of chlorine, and its addition to another. Thus $2(KO,ClO) = KCl + KO,ClO_2, 2(KO,ClO_2) = KCl + KO,ClO_4$ ; or if we have potassa in excess, or even chlorine escaping, and so the oxygen increasing in the acid, there can be no difficulty in understanding the tendency to the formation of the more stable chloride and chlorate, instead of the chloride and weak hypochlorite. The compound with lime and chlorine seems more permanent; still, on being exposed to the air (the carbonic acid of the air), it is decomposed, a carbonate formed, and hypochlorous acid and chlorine evolved. In preparing the bleaching powder, chlorine (evolved generally from peroxide of manganese, and the muriatic acid which runs from the condensers of alkali works) is passed into brick chambers, in which the hydrate of lime is arranged on shelves.

Bleaching powder is soluble in about 10 parts of water.

## CHLORIMETRY.

The amount of chlorine in bleaching powder is estimated by the amount of protosalt of iron which the chlorine disengaged from it can peroxidise. This depends upon the decomposition of water when chlorine is evolved in contact with such a salt of iron, the formation of muriatic acid, and evolution of oxygen, which goes to the iron. And as the protoxide of iron is FeO, and the peroxide $Fe_2O_3$, it follows that $2FeO + HO + Cl = Fe_2O_3 + ClH$, or one equivalent of chlorine will peroxidise two equivalents of a salt of iron—*i. e.*, 35·5 of chlorine will peroxidise 152 grains of pure protosulphate of iron. But this salt contains water of crystallisation, and, in practice, 10 grains of chlorine are found to be capable of peroxidising 78 grains of the crystallised sulphate. In order to perform this analysis, the protosulphate is powdered, and dried by pressure between blotting paper. In testing for chlorine, 78 grains of this salt are dissolved in two ounces of water. Fifty grains of the chloride of lime are dissolved in the same quantity of warm water, and poured into the alkalimeter, which is filled up to 0 on the scale by the addition of water, and the whole well mixed. The solution is then poured into the solu-

tion of sulphate, till the latter is completely peroxidised, and the number of measures of chloride requisite to produce this effect observed. The change is discovered by the effect of red prussiate of potass, which gives a blue precipitate with the protosalt of iron, but not with the persalt; so that, as soon as the iron ceases to be peroxidised, this blue precipitate is observed. A few drops of the solution may, from time to time, be dropped on a porcelain plate; as soon as the blue colour is manifest, then the saturation is complete. Of course, the more chlorine the specimen contains, the less is the quantity of it required to peroxidise the iron. Thus, as the number of measures poured out of the alkalimeter is to 10 grains of chlorine, so is 100 of the chloride to the whole amount of chlorine; or, as 50 grains, instead of 100, of the chloride have been employed, the percentage will be obtained by doubling the quotient.

Tests for Lime.—Lime is distinguished from the somewhat similar bodies, baryta and strontia—1st, by the action of sulphuric acid on very dilute solutions; from such, baryta and strontia are immediately precipitated as sulphates, while no precipitate is produced with lime; 2nd, by the action of oxalic acid, which readily precipitates very weak solutions of salts of lime, and does not so easily precipitate the salts of baryta and strontia; nor is the precipitate easily soluble in muriatic or acetic acid. Lastly, salts of baryta give a greenish colour to flame; those of strontia a red, and those of lime communicate a purple hue.

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## 21. MAGNESIUM, Mg.

Eq. 12·2. This metal is obtained by heating sodium, covered with small fragments of dry chloride of magnesium, in a tube of Bohemian glass. Ignition takes place, and the chloride of sodium is formed. It can be washed out with a little water, and the metal is left behind in small globules, which can be fused, when strongly heated, covered with a layer of chloride of potassium, and made to run together. The metal is as bright as silver, malleable, capable of being crystallised in octohedrons. In moist air it is tarnished; heated to redness, it burns, and forms magnesia.

### Magnesia, MgO.; Eq. 20·2;

Is prepared by simply heating the carbonate just as lime is prepared. Its sp. gr., after being ignited, is 3·61; but, in the ordinary form, much lighter. When precipitated from one of its soluble salts—as, for example, the sulphate—it forms a hydrate, which is much less soluble in cold water than even lime, requiring, it is said, more than 5000 parts of water at 60° to dissolve it, and is still less soluble in boiling water. Its solution, however, has an alkaline reaction. As its salts are comparatively harmless, it is a useful antidote to the acid poisons, and also to arsenious acid.

### CHLORIDE OF MAGNESIUM, MgCl.; Eq. 47·7,

Exists in sea-water, and often with chloride of calcium in mineral waters. It can be readily prepared by neutralising hydrochloric acid with magnesia, and, on evaporating, the solution can be obtained in acicular, very deliquescent crystals. Anhydrous chloride of magnesium, used in preparing magnesium, is best prepared by taking two equal quantities of muriatic acid, and neutralising each, one with magnesia, and the other with ammonia, mixing them, and evaporating the mixture to dryness, whereby a double chloride of ammonium and magnesium is formed. On heating this to dryness, the ammoniacal salt is driven off, and fused chloride of magnesium is left behind.

Other haloid salts of magnesium may be formed, also a sulphuret.

*Carbonate of Magnesia.*—$MgO,CO_2$, Eq. 50·2; exists in nature in the form of the mineral magnesite. It may be obtained anhydrous by a difficult process, or as a hydrate by mixing solutions of soluble salts of magnesia and carbonate of potash at the boiling point. The precipitate is to be diffused in distilled water, and carbonic acid passed through the liquid On allowing the solution of supercarbonate of magnesia which is formed to evaporate spontaneously, the excess of carbonic acid which had kept the carbonate in solution gradually escapes, and the carbonate is deposited in hexagonal crystals. These crystals contain 3 eq. of water, of which they lose two when exposed to the air.

Prepared by simply precipitating, as above described, by mixing the solutions of carbonate of potass and (say) sulphate of magnesia, the carbonate contains 4 eq. of magnesia, 3 of $CO_2$, and 4 HO. Thus obtained, it should be well washed for use. It occurs in two forms, the light and heavy; the latter is prepared by the mutual action of hot solutions of carbonate of potass and sulphate of magnesia, as described; but they are evaporated to dryness, and the residue well washed.

*Sulphate of Magnesia*, Epsom salts, $MgO,SO_3,HO + 6HO$, Eq. 60·2+63—Exists in most natural waters, and in large quantities in some, as, for instance, that of Epsom. It is usually obtained from two sources—1st, From the bittern of sea water, the constituents of which are chiefly muriate and sulphate of magnesia; to this sulphuric acid is added so as to convert the whole into a sulphate. 2nd, The more usual way is to burn magnesian limestone, a compound of carbonate of lime and magnesia, and treat this with sulphuric acid, when the mixed sulphates of lime and magnesian are easily separated by their very different degrees of solubility. The formula given above is that of the crystals; they are soluble in an equal weight of water at 60°.

*Phosphate of Magnesia* is formed when cold solutions of the common phosphate of soda and sulphate of magnesia are mixed and allowed to stand for a day. It separates in small prismatic crystals.

*Phosphate of Magnesia and Ammonia, or Ammoniaco Magnesian Phosphate*, $2MgO,NH_4,O,PO_5+12HO$, on the ammonium theory—Is formed when a tribasic phosphate is mixed with a salt of magnesia, and

either ammonia or its carbonate added. A crystallised precipitate gradually subsides, and more quickly on slight concentration. This salt is insoluble in saline solutions, and somewhat soluble in pure water. Magnesia is often separated from its solutions by means of this salt. The presence of the ammoniaco magnesian phosphate in the urine is often of great consequence in disease.

*Silicates of Magnesia.*—Many of these exist as minerals in nature.

The best tests for magnesia are, that its salts yield the bulky white precipitates of the oxide with the caustic alkalies, which are not soluble in excess of the reagent, but soluble in solution of muriate of ammonia. Then, with solution of phosphate of soda, or the addition of ammonia, they give the crystalline ammoniaco magnesian phosphate (found in urine). Lastly, they give precipitates with the carbonates of potass and soda; but none in the cold with carbonate of ammonia.

Sect. 3. METALLIC BASES OF THE EARTHS. These are, Aluminum, Glucinum, Zirconium, Yttrium, Terbium, Erbium, and Thorium.

## 22. ALUMINUM, Al.

Eq. 13·7.; sp. gr. 2·6. Is obtained by a process analogous to that employed for the preceding metal. This metal is malleable, and requires a very high temperature to melt it.* It has a slight action on boiling water, being partially oxidated, and disengaging hydrogen. When heated in the air, it burns and forms alumina.

### ALUMINA, OXIDE OF ALUMINUM, $Al_2O_3$; Eq. 51·4.

It is in this proportion that aluminum enters into combination both with oxygen, and with chlorine, bromine, &c. It exists native, almost pure, in the sapphire and ruby. It may be obtained in two forms by different methods:—1st, When sulphate of alumina and ammonia is ignited, all the sulphuric acid and ammonia are driven off, and a residuum is obtained insoluble in acids. 2nd, When the sulphate of alumina and potass (alum) is dissolved in boiling water, and the solution treated with ammonia, or its carbonate, it is thrown down as a white gelatinous precipitate. This being washed and dried, is found to be a hydrate, quite insoluble in water, but soluble in acids. It is also soluble in potash, and is precipitated from this solution exposed to the air, in crystals. Alumina is without taste; it absorbs moisture from the air. It is fused by the oxyhydrogen blow-pipe. One of its most remarkable properties is its affinity for organic colouring matters, which it withdraws from their solutions. On this account

* These properties are worthy of note, on account of the resemblance between aluminum and iron.

its salts are largely employed in dyeing, and have the power of fixing the colour in the cloth; they are called *mordants.* Other metallic bases have similar properties.

This power has been regarded by some as a species of cohesive attraction, similar to that by which charcoal removes colouring matters from their solutions; but in the case of alumina, at least, it seems to be owing to a chemical action, for alumina has a much stronger affinity for one kind of colouring matter than another. The action must be so managed as that, from a solution of the colouring matter and a solution of a salt of alumina, a precipitate of the colouring matter and an insoluble salt of alumina, or the earth itself, may be thrown down with or without the addition of a reagent. Thus a solution of common alum and the colouring matter may be mixed, and a solution of an alkaline carbonate added, when alumina will be thrown down as a hydrate along with the colouring matter; or, generally, the acetate of alumina is used, because at a boiling temperature a basic acetate of alumina is precipitated from a solution of the salt and the colouring matter, which carries the latter along with it, and thus is capable of fixing it in cloth.

### Chloride of Aluminum, $Al_2Cl_3$, Eq. 133·9.

Is prepared by dissolving alumina in muriatic acid. The solution concentrated crystallises with 10 eq. of water, or forms, on being evaporated to dryness, a deliquescent mass, which, heated strongly, evolves chlorine, leaving alumina behind. To obtain the anhydrous chloride, pure alumina is calcined in a crucible with oil and lamp-black. This is to obtain the alumina free from water, and intimately mixed with carbon. It is then exposed in a porcelain tube to the action of a current of dry chlorine gas, at a red heat. The theory of what takes place is expressed by the formula, $Al_2O_3 + 3Cl + 3C = 3CO + Al_2Cl_3$; or, chloride of aluminum is formed, and the oxygen of the alumina combines with a portion of carbon to form carbonic oxide gas. The chloride is found at the cool extremity of the tube, or in another tube fitted into it, in acicular crystals. It is very deliquescent.

*Sulphate of Alumina,* $Al_2O_3$, $3So_3 + 18HO$. Eq.; $171·4 + 162$.— This salt is obtained by the action of sulphuric acid on alumina. Its solution, concentrated, crystallises in thin pearly plates. They are soluble in two parts of water. When heated, it melts at first in its water of crystallisation, but by a red heat the water and acid are expelled, and alumina remains. This salt has the sweet and astringent taste of alum. It is principally remarkable for being the basis of the important double salt, the

*Sulphate of Alumina and Potass,* $KO,SO_3 + Al_2O_3, 3SO_3 + 24HO$; Eq. $258·4 + 216$.—This salt may be prepared in the laboratory by mixing strong hot solutions of sulphate of alumina and sulphate of potass, when crystals of alum are formed on the cooling of the liquid. It is prepared in commerce by various processes. In the first place, it occurs native in Italy, and is procured by simply lixiviating the rock in which it exists. It is generally made from a clayey slate called

alum shale. Here it is combined with silica and iron pyrites (sulphuret of iron). The ore is roasted, and then exposed to the action of air and moisture. The excess of sulphur in the pyrites is converted into sulphuric acid, which combines with the alumina, while the eq. of sulphur which still remains in it is oxidated as well as the iron, so that $Fe_2S + O_7 = FeO, SO_3 + SO_3$. The sulphuric acid thus disengaged, acts on other bases as well as alumina, which are contained in the slate. The mass, after this action has taken place, is lixiviated. The solution is evaporated, and generally the sulphate of iron which it contains is crystallised out for use. Solution of chloride of potassium is then added; this exchanges its hydrochloric acid for the sulphuric acid of the other sulphates, and the sulphate of potass, thus formed, combines with the sulphate of alumina. The chlorides formed are much more soluble than the alum, which can be separated by crystallisation. Alum crystallises in regular octohedrons, with truncated spires. Its water of crystallisation is driven off by heat, and the *aluminum ustum* of the pharmacopœia remains. Alum is soluble in 18 parts of water at 60°.

Ammonia and soda can replace potassa in alum without change of form in the crystal, and sesquioxide of iron can similarly replace alumina. These facts offer striking illustrations of isomorphism.

*Silicates of Alumina.*—Clays are silicates of alumina; some of them, and some minerals, approach very near to definite chemical compounds of silicic acid and alumina. Thus feld-spar contains a silicate of alumina $Al_2O_3,SiO_3$, and kaolin, the purest kind of clay used for the making of porcelain, consists principally of the same compound in a hydrated form. The silicate of alumina is the essential basis of pottery. It owes this useful property, which it possesses in the form of clay, in the first place principally to the facility with which it can be moulded in the moist state, and to the fact that it can be dried without cracking, as its water is driven off; and, in the second place, to its power of forming a semivitrified substance when a strong heat is applied. The presence of other bases, as soda, potass, or lime, may cause the pottery to become more vitreous, from their greater tendency to form glasses with silicic acid. This is the way in which porcelain is produced, instead of the ordinary pottery. After pottery has been sufficiently hardened, it is dipped into some fused vitreous substance, and then heated in a kiln to glaze it.

23—28. GLUCINUM, YTTRIUM, ERBIUM, TERBIUM, THORIUM, and ZIRCONIUM, are found in the form of earths in some rare minerals. Glucinum closely resembles aluminum, and its oxide, which exists in the beryl and emerald, has the formula $Gl_2O_3$. Yttrium as YO exists in the mineral gadolinite. It is there associated with erbia and terbia, the bases of erbium and terbium. The oxide of thorium is ThO, while that of zirconium is $Zi_2O_3$; so that of these bodies glucinum and zirconium bear more analogy to aluminum, and the others to magnesium.

Sect. 4.—METALLIC BASES whose Protoxides are Isomorphous with Magnesia.

These belong to the class of metals proper, inasmuch as the metallic properties are more fully developed in them. They are, Manganese, Iron, Cobalt, Nickel, Zinc, Cadmium, Copper, and Lead.

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## 29. MANGANESE, Mn.

Eq. 27·67; sp. gr. 7·05. This metal exists abundantly in nature in various ores, in combination with oxygen.

The metal itself is best obtained by heating the carbonate of the protoxide in a closed crucible, so as to expel its carbonic acid—see fig. 31.
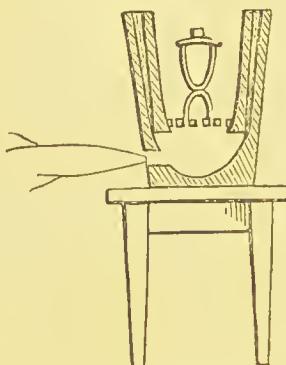


Fig. 31 shews a blast furnace, made of two black-lead crucibles, termed blue pots. The bottom of one is cut off. It is then placed within the other, and the interstitial space filled up with luting.

Fig. 31.

The oxide which remains is then to be mixed with oil and powdered charcoal, and put into a crucible lined with charcoal, which is to be heated in a wind furnace, as in fig. 30, or, better still, a blast furnace, as in fig. 31. After this operation has been continued for some hours in the wind furnace, and a shorter time in the blast furnace, some pieces of manganese will be found at the bottom of the crucible; but as these are combined with a little carbon; in order to obtain the pure metal, they must be treated with carbonate of manganese and borax.

Manganese is, in many respects, very like iron; but with a much greater affinity for oxygen,—so much so, that it should be kept in sealed tubes. It decomposes water at the boiling point, with evolution of hydrogen, and, of course, readily, when acids are added, forming salts.

Manganese forms several compounds with oxygen. Several of these exist in nature, either pure or mixed in various ores of manganese; but those which have a distinct chemical existence are the Protoxide—the basis of the salts MnO; the Sesquioxide, which is formed

when the peroxide is heated in vessels, $Mn_2O_3$; the Peroxide, of so much importance in commerce, $MnO_2$; Manganic acid, $MnO_3$; and Hypermanganic acid, $Mn_2O_7$.

### PROTOXIDE OF MANGANESE, MnO ; Eq. 35·67;

Is obtained pure by passing a stream of hydrogen over the carbonate at a red heat. In the air it absorbs oxygen. It is thrown down as a hydrate when its salts in solution are treated with alkalies. This oxide forms the stable salts of manganese.

### SESQUIOXIDE, $Mn_2O_3$; Eq. 71·34;

Exists in the minerals *braunite* and *manganite*. It forms some salts, generally unstable; the most remarkable of which is the sulphate $Mn_2O_3,SO_3$, which can be substituted for sulphate of alumina or persulphate of iron in combination with sulphate of potass, so as to form a manganese alum.

A red oxide, a combination of the protoxide and sesquioxide, *is said to be formed* when oxides of manganese are heated in the open air, and occurs in nature in the mineral called *Hausmannite*.

### PEROXIDE, BINOXIDE, OR BLACK OXIDE OF MANGANESE, $MnO_2$; Eq. 43·67;

Exists abundantly in nature, and is sometimes found almost pure in radiating prismatic crystals. It is often found associated with other minerals, and especially with compounds of lime, baryta, and iron. The most serious impurity for ordinary chemical purposes which it can have, is the presence of an earthy carbonate. From this it may be freed when the carbonate is in small or moderate quantity, by washing with a dilute acid. It may be obtained in the form of hydrate by adding a solution of chloride of lime to a solution of sulphate of manganese. Here the chlorine evolving oxygen acts as an oxidising agent. When heated in close vessels it gives off oxygen, and becomes the sesquioxide, as already described (see Oxygen), and, in contact with sulphuric acid, it forms sulphate of the protoxide. Heated with caustic potass in a close vessel, it forms a manganate of potass, and the sesquioxide; for $3MnO_2 + KOHO = KO,MnO_3 + Mn_2O_3 + HO$; but if oxygen be present, *i. e.*, if the two substances be heated in the open air, the whole of the peroxide is converted into manganic acid, and combines with the potass.

This substance is much used in glass-making, for it fuses readily with the other materials used in the manufacture of glass, and gives a slight purple hue to the material, which improves its colour. Its extensive use in the manufacture of bleaching powder (see Chlorine, Chloride of Lime), renders it very important, as it occurs in commerce in ores more or less impure, to ascertain its value, or, in other words, the per-centage of peroxide which the ore contains. For this purpose, a common way is to take the amount of protosulphate of iron which it can peroxidise when treated with muriatic acid. Fifty grains of

peroxide of manganese treated with excess of muriatic acid, if perfectly pure, should peroxidise 317 grains of protosulphate of iron, carefully dried by pressing it between folds of blotting-paper; and by whatever proportion the amount peroxidised falls short of that quantity, by so much is the peroxide impure. The protosulphate is added by degrees to the muriatic acid and manganese, heated in a flask until there is no odour of chlorine evolved, and the solution gives a blue precipitate with solution of red prussiate of potass. Whatever remains of the protosulphate will bear the same proportion to the 317, as the peroxide contained impurity in 100.

## MANGANIC ACID, $MnO_3$,

Only exists in combination with bases. A solution of the manganate of potass is best prepared by heating a paste of equal parts of hydrate of potass, and peroxide of manganese, in a tube, through which a current of oxygen is passed. A green solution of manganate of potass may be obtained from this. Excess of water decomposes the manganate, causing the precipitation of peroxide of manganese, and the formation of permanganate of potass, which forms a purple solution. The ready change from the green manganate to the purple permanganate has caused this substance to be styled the mineral chameleon.

## CHLORIDE OF MANGANESE, $MnCl$; Eq. $63\cdot17$:

Remains after the preparation of chlorine from the action of muriatic acid on peroxide of manganese. The residue evaporated to dryness, then redissolved and allowed to crystallise, yields four sided-tabular crystals of this salt, which contain six equivalents of water. When heated, this water is expelled, and an oxide of manganese is left. Bromides and iodides of manganese are formed by the action of hydriodic or hydrobromic acid on the peroxide. The sulphuret is not thrown down by the action of sulphuretted hydrogen on a solution of salt of manganese; but is precipitated by hydrosulphate of ammonia.

*Carbonate of Manganese* is formed when an alkaline carbonate is added to a protosalt of manganese in solution.

Salts of the protoxide of manganese give white precipitates, which soon become brown, insoluble in excess of the re-agent, with the caustic alkalies. With the alkaline carbonates, the white precipitate does not soon change colour. The yellow prussiate of potass gives a white precipitate. The oxide of the metal gives at the blow-pipe heated with borax, an amethystine bead in the outer flame, and a colourless one in the inner flame.*

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* The outer flame of the blow-pipe as in the diagram of flame, is termed the oxidising flame, on account of the near presence of air, and absence of unconsumed inflammable matter. The inner flame, containing unconsumed inflammable matter, is the deoxidising or reducing flame, because this inflammable matter takes oxygen from many oxides exposed to it.

## 30. IRON, Fe. (Ferrum.)

Eq. 28; sp. gr. 7·8. Irou rarely occurs native; but it exists in the stones called aerolites. In combination it occurs everywhere; hardly a rock but owes any colour it may possess to the presence of iron. It exists in many waters; in plants; and forms, it is believed, an essential ingredient of the blood of animals.

Pure iron may be obtained, for chemical purposes, by putting four parts of fine irou wire, cut in small pieces, along with one part of the protoxide of iron, into a Hessian crucible. These are to be covered with powdered green glass, containing uo lead; the crucible is to be then covered and exposed to the heat of such a furnace as represented in fig. 30. The object of this process is to free the iron from some carbon and silicon which the wire contains; for this purpose the oxygen of the protoxide is the agent; it oxidises these bodies, while the glass serves as a flux, and at the bottom of the crucible there will be found a button of pure iron. In this form the iron is white, and shiues like silver. It is soft and tough.

Another mode of obtaining iron is to precipitate the sesquioxide from the sesquichloride by means of ammonia, and to heat this oxide, well washed and dried, in a current of hydrogen. In this form it is a dark-grey powder, possessed of some of the catalytic influence of spongy platinum.

Irou is remarkable for its tenacity and malleability, properties, to which is owing, in great part, its immense utility to mankind.

Iron is obtained, commercially, almost invariably by a very different process. The ores of iron used, consist for the most part of compounds or mixtures of oxide, or carbonates of iron with silica and alumina. The object is to form a fusible slag, which will coutain the impurities in the ore. For this purpose limestoue is used, which forms a kind of glass, a silicate of lime and alumina, readily fusible; it also forms a medium whereby the carbon or coal generally used to reduce the iron from its state of oxide, may more readily act. The iron, in the form of carburet, falls through the slag, and is drawn off from time to time.

Iron obtained in this way is called cast-iron. Its specific gravity is less than that of pure iron, and, besides carbon and silicon, it contains traces of mauy earths and bases. It is purified by a process called puddling, which consists essentially in heating it in a kind of reverberatory furnace, and stirring it so as to expose it to the oxidating influence of the air. In this way most of the impurities are burnt off, while the silicic acid forms a flux. It is afterwards rolled or formed into bars, and in this state is called malleable irou.*

* The process consists of two parts, *refining*, and *puddling*. In the former the cast-iron is kept in fusion, exposed to a strong current of air, and stirred; some of the oxide of iron formed, becomes a glass with the silica. It is then run into cold water, while in the melted state. It is then transferred into the puddling furnace, where it is again fused, and collected into masses, which are hammered and rolled.

Steel is iron containing about 1·5 per cent. of carbon—a little more or less. It is prepared by a process, called cementation. Bars of the purest iron are imbedded in charcoal, in crucibles adapted to the purpose, and exposed to intense heat. Besides carbon, it generally contains small quantities of silicon and phosphorus. It is harder than iron, and of about the specific gravity. Its useful properties are well known.

Iron, as prepared by the hydrogen process, will take fire in the air. Pure water has no action on bright pure iron, unless free oxygen is present; nor does dry air affect it; the *rusting* takes place most readily when iron is exposed to moist air. This rust is a hydrate of the sesquioxide. At a red heat it takes oxygen from water, as has been seen, and forms the protoxide. Iron is magnetic until it is strongly heated.

There are three chemical compounds of iron with oxygen—the Protoxide, $FeO$; the Sesquioxide or Peroxide, $Fe_2O_3$; and a compound, represented by the formula $FeO_3$, called ferric acid.

### PROTOXIDE OF IRON, $FeO$; Eq. 36.

This oxide is thrown down when pure potassa is added to a solution of protosalt of iron. It, however, rapidly absorbs oxygen, and passes into the state of peroxide. Its salts have the same tendency to absorb oxygen, so that it is almost impossible to obtain them or it pure.*

### SESQUIOXIDE OF IRON, $Fe_2O_3$; Eq. 82.

This oxide exists in nature abundantly under the name of hematite. It may be prepared by adding ammonia to solution of the persulphate. The iron is thrown down under the form of hydrate. If this be collected, washed, dried, and ignited, a brownish substance remains—the sesquioxide of iron. It may also be prepared by heating the sulphate of the protoxide (copperas) by a strong red heat for some time. Decomposition of the sulphuric acid takes place, sulphurous acid is disengaged, and oxygen afforded, so to convert two equivalents of the protoxide into one of peroxide, or $2FeO + O = Fe_2O_3$. Obtained by the former of these processes, the hydrated peroxide is an antidote to arsenic, with which it forms the arsenite of iron, a body almost harmless. Prepared in the second way, on the large scale, it forms a pigment known as Venetian-red. This oxide dissolves readily in acids forming salts.

### MAGNETIC OXIDE OF IRON, $Fe_3O_4$, OR BLACK OXIDE,

Is a mixture of the other two oxides; it exists in nature in octohedral crystals, which have magnetic properties, as is well known. It is formed when the sesquioxide is heated to whiteness. It is prepared by mixing solutions of protosulphate and persulphate of iron in such proportions as that 1 eq. of each may be present, and precipitating them by ammonia, or

$$FeO,SO_3 + Fe_2O_3,3SO_3 + 4(NH_3HO) = FeO + Fe_2O_3 + 4(NH_3,HO,SO_3)$$

* This is the oxide isomorphous with magnesia.

and $FeO + Fe_2O_3 = Fe_3O_4$.  The hydrated magnetic oxide thus obtained is dark-green, and is attracted by the magnet.  The black scales disengaged by smiths in forging iron approach this oxide in composition.  This oxide dissolves in acids, and forms, as tests show, salts of the protoxide and sesquioxide.  It therefore has no proper salts.

### FERRIC ACID, $FeO_3$.  Eq. 42.

This substance can be obtained in combination by heating one part of sesquioxide of iron with four of dry nitre in a covered crucible, at a full red heat, for an hour.  The mass, when treated with cold water, gives a fine purplish red solution of ferrate of potass.  But this rapidly decomposes in the air, evolving oxygen and precipitating sesquioxide of iron.

#### CHLORIDES OF IRON.

There are two—the Protochloride, corresponding to the protoxide; and the Perchloride, to the sesquioxide.

### PROTOCHLORIDE OF IRON, $FeCl$; Eq. 63·5;

May be obtained anhydrous by heating iron wire in a tube, at a red heat, and passing a current of muriatic acid gas over it.  The mass melts, and, on cooling, crystallises.  It is volatile at a high temperature.  It is also formed by dissolving iron in muriatic acid.  When the solution is evaporated it yields crystals, which contain 4 eq. of water, are very soluble, and, when exposed to the air, soon become peroxidised.

### PERCHLORIDE OF IRON, $Fe_2Cl_3$; Eq. 152·5.

This compound may be obtained by heating iron wire, as in the preceding process, in an atmosphere of chlorine; or it may be prepared by dissolving the sesquioxide in muriatic acid.  When the solution is evaporated until it becomes syrupy, it yields reddish-yellow scaly crystals.  Evaporated to dryness, it is partially decomposed, partly sublimed, in the form of red crystals.  This compound is soluble in alcohol.

#### BROMIDES AND IODIDES OF IRON.

These compounds correspond to the chlorides, and may easily be formed directly by the action of bromine and iodine on iron.  All that is necessary, is to mix the bromine or iodine with iron, in the proper proportions, in the presence of water, and apply a very gentle heat, and either a protocompound or a percompound, a protobromide, or a perbromide, will be formed.  There is great difficulty in keeping these protocompounds in the state of protosalt, they having a tendency to pass into persalts, and to throw down sesquioxide of iron.  This it was attempted to prevent formerly by keeping metallic iron in their solutions, so that when the peroxide of iron was precipitated, and iodine or bromine disengaged, it might have some iron to act upon, and thus a fresh protosalt be formed, and the protosalt, in fact, renewed as long as iron

was present.   But as it is an object, for medicinal purposes, to retain
these salts, and especially the iodide, in the state of protosalt, this is
now accomplished by keeping the preparation in the form of syrup—
for sugar has a tendency to restrain the protosalts of iron from passing
into the state of persalts.   According to the process of the Edinburgh
Pharmacopœia, six fluid ounces of a syrup so prepared, simply by add-
ing sugar in solution to solution of iodide of iron, would contain 4½
ounces of sugar to 240 grains of iodide of iron.   Solution of protoiodide
of iron, evaporated to dryness, melts, and yields a somewhat crystalline
mass, which soon deliquesces.

### SULPHURETS OF IRON.

The sulphurets of iron do not exactly follow the law of the oxides.
There are, at least, four definite compounds, besides subsulphurets,
which may be prepared by particular processes.   These are, the Proto-
sulphuret, $FeS$; the Sesquisulphuret, $Fe_2S_3$; the Bisulphuret, $FeS_2$;
and the Tersulphuret, $FeS_3$.

### PROTOSULPHURET OF IRON, $FeS$; Eq. 42;

May be prepared by the direct union of iron-filings and sulphur,
assisted by heat, in the proper proportions, or rather a very
slight excess of sulphur may be used—a little of it being volatilised
before combining with the iron.   This compound is principally used
for the preparation of sulphuretted hydrogen.   For practical purposes,
2½ parts of sulphur and four of iron-filings, well mixed, may be cast
into a red-hot crucible, when they will combine, and form, as nearly as
possible, a protosulphuret of iron.   When treated with sulphuric or
muriatic acid, this compound gives off sulphuretted hydrogen gas.
The reaction with the former acid has been described under the head
of sulphuretted hydrogen.   With the latter it is simply the substitu-
tion of chlorine for sulphur in combination with iron, and the hydrogen
of the muriatic acid of the chlorine combining with the sulphur of the
sulphuret—thus $FeS + ClH = FeCl + SH$.   This sulphuret of iron is
thrown down as a hydrate when solutions of protosalts of iron are
treated with hydrosulphate of ammonia, for they will not give a pre-
cipitate with sulphuretted hydrogen alone.   When this sulphuret is
exposed to the air and moisture, it is converted, by absorption of
oxygen, into sulphate of the protoxide, and considerable heat is
evolved.   This is supposed often to be the origin of the spontaneous
combustion of coal, in which this sulphuret exists in the mineral state.

SESQUISULPHURET OF IRON, $Fe_2S_3$, is obtained as a black precipi-
tate, when a solution of a persalt of iron is added to an alkaline
sulphuret.

### BISULPHURET OF IRON, $FeS_2$;   Eq. 60.

This substance, under the name of iron pyrites, is well known.   It
occurs abundantly in nature, and is often found in yellow beautifully
regular, cubical, and dodecahedral crystals.   When this substance is

heated in the open air, it gives off its sulphur, and leaves the red oxide of iron; when heated in closed vessels, it is converted into another sulphuret, which, from its properties, is termed the magnetic, $Fe_7S_8$, and which occurs also in nature. The bisulphuret is not acted upon in air like the protosulphuret. $FeS_3$ is believed to be obtained when sulphuretted hydrogen is passed into a solution of ferrate of potassa.

Compounds of iron of a more or less determinate character with carbon, boron, phosphorus, silicon, &c., may be formed.

## COMPOUNDS OF IRON WITH ACIDS.

*Carbonate of Iron*, $FeO,CO_2$; Eq. 58.—This substance occurs as a very abundant ore. It is prepared when a solution of a protosalt of iron is decomposed by an alkaline carbonate. Thus, when solutions of protosulphate of iron and carbonate of soda are mixed, then $NaO,CO_2 + FeO,SO_3 = FeO,CO_2 + NaO,SO_3$. It is at first a white hydrate, but, when exposed to the air, it rapidly becomes green, and then brown, losing its carbonic acid, and being converted into a hydrate of the magnetic oxide. To prevent this, and retain it in the form of a protosalt of iron, which is very important for medicinal purposes, the fresh precipitated hydrate is washed, and the water squeezed out, and immediately triturated with fine powdered sugar, and dried at a temperature not exceeding 100°.

*Sulphates of Iron.*—The protosulphate $FeO,SO_3$, Eq. 76, is readily prepared in the laboratory by dissolving iron filings in dilute sulphuric acid; hydrogen is disengaged, the iron oxidised, and the sulphuric acid combines with it. In commerce it is prepared by exposing the protosulphuret or magnetic sulphuret to the action of air and moisture. For this purpose pyrites is calcined to expel excess of air and moisture, and exposed to the atmosphere on beds or terraces formed on some bank, called copperas beds. After some time, water, if necessary, is run over these beds, and the lixivium evaporated until the crystals are formed. These crystals are oblique rhomboidal prisms, whose formula is $FeO,SO_3HO+6HO$. The latter 6 eq$^s$. of water are driven off at 212°, leaving a hydrate of the sulphate. When heated much further, the salt begins to be decomposed as described under peroxide of iron.

When a solution of the protosulphate is exposed to the air, sesquioxide of iron forms, and is precipitated with sulphuric acid; oxygen is absorbed from the air, and a persulphate is formed $Fe_2O_3,3SO_3$.

There are numerous compounds of iron with other acids, some of the more important of which may be referred to under the head of

## TESTS FOR IRON.

1. When a solution of the yellow prussiate of potass, or ferrocyanide of potassium, is added to a solution of a protosalt of iron, of 4 eq$^s$. of potassium in 2 eq$^s$. of the former salt, 3 are replaced by the iron, $2(K_2FeCy_3) + 4(FeO,SO_3) = Fe_3KFe_2Cy_6 + FeO,SO_3 + 3(KO,SO_3)$. The first compound is the bluish white precipitate that falls; ex-

posed to the air it absorbs oxygen, and becomes blue. It then yields the prussiate of potass to water, and after being washed a compound remains of one equivalent of prussian blue with one of peroxide of iron. Thus, if we double $Fc_3K,2(FeCy_3)$ and remove from it one equivalent of ferrocyanide of potassium, $K_2(FcCy_3)$ there will remain $Fc_63(FeCy_3)=Fe_43(FeCy_3)+Fc_2O_3$,—the 3 of oxygen being obtained by absorption from the air.

2. Again, when the red prussiate of potass, or ferricyanide, is added to a solution of a protosalt of iron, then 3 of iron are simply substituted for 3 of potassium, in the ferricyanide, or $3K(Fe_2Cy_6)+3(FeO, SO_3)=3(KO,SO_3)+3Fe,2(FcCy_3)$. This precipitate is very similar to prussian blue, but may be distinguished from it by boiling in solution of yellow prussiate of potass, when it gives again the red prussiate, which prussian blue does not. This is called Turnbull's blue.

3. When prussiate of potass is added to a persalt of iron, prussian blue is formed. The formula of this substance is $Fe_4,3(FeCy_3)$, and its formation is thus explained — $3(K_2,FeCy_3,)+ 2(Fe_2O_3,3SO_3) = 6 (KO,SO_3) + 4Fe,3(FeCy_3)$.

4. Infusion of galls gives a black precipitate with the persalts of iron.

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## 31. COBALT, Co.

Eq. 29·5, sp. gr. 8·5, occurs in nature, for the most part allied with arsenic, as an arseniuret, or with sulphur and arsenic, as $CoAS + CoS_2$, and alloyed with nickel iron. Cobalt also exists in the aerolites.

To obtain cobalt from the arseniuret and sulphuret, it is roasted, an impure oxide of cobalt, known as *zaffre*, remains. This is dissolved in muriatic acid, and a portion of remaining arsenic is separated by passing sulphuretted hydrogen through the liquid; the filtered solution is then boiled with a little nitric acid to peroxidise any iron present, and carbonates of iron and cobalt thrown down by the addition of an alkaline carbonate. The precipitate is acted upon by oxalic acid, oxalates of iron and cobalt are formed, of which the former is soluble, and can be removed by washing, while the latter remains, is dried and heated to redness in a covered crucible. The oxalic acid is decomposed, and its carbon assists in reducing the cobalt to the metallic form. If nickel is associated with the cobalt, it will be found mixed with the oxalate of cobalt in the form of oxalate of nickel. To separate them, the mixed oxalates are dissolved in ammonia, and the mixture diluted exposed for some days in a shallow vessel to the action of the air; the ammonia gradually evaporates, and the salt of nickel precipitates, while that of cobalt remains. The liquid is then poured off the precipitate, and evaporated to dryness.

Cobalt is a metal of a greyish-red colour, more fusible than iron when pure; it is not now held to be magnetic. It is less easily

oxidated than iron; but dissolves readily in nitric acid. Like iron, it forms two oxides, $CO$ and $C_2O_3$.

### Protoxide of Cobalt, $Co$; Eq. $37\cdot57$;

Is obtained by igniting the carbonate. It is then a dark-grey substance. It is thrown down from its solutions by the addition of an alkali, of a fine blue colour. When melted with glass, it gives it a fine blue colour. This is called *smalt*. The salts of this oxide are of a red colour. They are acted upon by alkaline sulphurets like those of iron. Magnesia, when heated with a drop of the nitrate of cobalt before the blow-pipe, gives a fine pink colour. Cobalt forms a compound with oxide of aluminum. When solutions of alum and cobalt mixed are precipitated with an alkaline carbonate, a precipitate of a beautiful blue colour is formed.

The Chloride of cobalt is formed by dissolving the oxide in muriatic acid. Its red solution is used as a sympathetic ink, characters written with it not being visible till the paper on which it is inscribed is heated. The Peroxide of cobalt is obtained by igniting the nitrate, not using a very high temperature; or by passing a current of chlorine through water, in which the carbonate is suspended. The carbonate, or rather subcarbonate, is procured by mixing hot solutions of a cobalt salt, and an alkaline carbonate. The sulphate closely resembles the sulphate of iron.

The principal use of cobalt is as a pigment; for this purpose, either smalt is used in a very fine powder, or what is termed Thenard's blue, which is prepared by adding phosphate of soda to solutions of cobalt and alumina, and calcining the precipitate.

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### 32. NICKEL, Ni.

Eq. $29\cdot42$; sp. gr. 85. Nickel exists in the meteoric stones; in these and its ores it is generally associated with iron and cobalt.

The most general source of nickel is from an arseniuret called *speiss*, which is formed in the preparation of smalt. Smalt is prepared by fusing zaffre, sand, and carbonate of potass together; a silicate of potass is formed, in which the oxide of cobalt dissolves, while the nickel, arsenic, and iron are found in a mass called speiss, at the bottom of the crucible. When powdered speiss is treated with an equal weight of sulphuric acid diluted with 4 or 5 parts of water, and an equal bulk of nitric acid added, it is dissolved, and the nickel and arsenic are oxidated. The solution, on being allowed to stand, deposits the latter in crystals. Carbonate of potass is then added, and the liquor concentrated, and set aside to crystallise. A double sulphate of nickel and potass forms, which, by another crystallisation, can be freed from arsenic. From a solution of this salt, the oxalate of nickel is thrown down by solution of oxalate of ammonia; and is washed, dried,

and ignited in the same way as the analogous oxalate for cobalt. It is found in this way in a spongy state; and to obtain it in a more metallic like form, this must be fused in a crucible covered with pounded glass.

Nickel is a very white metal, magnetic. It possesses the power of giving whiteness to its alloys; hence its use in German silver. It is rather more fusible than iron. It forms two oxides, corresponding to those of iron, $NiO$, $Ni_2O_3$. The PROTOXIDE may be prepared by igniting the carbonate, or by throwing it down from its salts by means of an alkali, as a dark-green hydrate. It is very soluble in acids, and in ammonia. All its salts have an intense green colour; they are precipitated by hydrosulphate of ammonia, which gives a black sulphuret. The PEROXIDE, $Ni_2O_3$, is formed in the same manner as the analogous compound of cobalt.

The *sulphate of nickel* crystallises in green prismatic crystals isomorphous with sulphate of magnesia.

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## 33. ZINC, Zn.

Eq. 32·31. This metal is found very extensively diffused in nature in the form of *calamine*, an ore of the carbonate, and zinc *blende* or *black jack*, a sulphuret; the latter form is generally associated with galina. The oxide, either from the roasted carbonate or the sulphuret, is heated with charcoal or coal, in a crucible, covered at top, and with a tube through its bottom, reaching some way into the interior of the crucible, and passing into a vessel containing water below; in this way the heavy vapour of the zinc descends, and is thus condensed. It may be purified by a second distillation, rejecting the first portions which come over, as they generally contain arsenic, lead, and cadmium; or the zinc may be obtained pure, by fusing it with one-fifth of its bulk of nitre. This forms arseniate of potass, which can be dissolved out, and the metal can be dissolved in dilute sulphuric acid, when the lead is left behind as an insoluble sulphate. Sulphuretted hydrogen passed through the solution of the zinc, in sulphuric acid, throws down the cadmium, but leaves the zinc, which can be thrown down as a carbonate by an alkaline carbonate. This, ignited and reduced in the same way as the ore was at first, gives pure zinc.

Zinc, as generally prepared, is of a bluish colour, with a crystalline structure. At temperatures between 212° and 400°, it is malleable, and can be rolled into sheets. Ordinary zinc has a sp. gr. of 6·8, but when rolled it acquires a sp. gr. of 7·2.

When zinc is heated to a red heat, it first melts a little below redness (773°). At a red heat it volatilises, and in an open vessel takes fire and burns with a brilliant greenish-white light, forming a large quantity of white fumes of oxide, termed philosophers' wool.

Exposed to the air and moisture it absorbs oxygen, then forms a

white film of oxide, which protects the remaining part of the metal. Zinc easily dissolves, in most acids, by substitution for hydrogen. There are three oxides of zinc—the Suboxide, $Zn_2O$; the Protoxide, $ZnO$; and the Peroxide, $ZnO_2$.

### SUBOXIDE OF ZINC.

This substance is not very clearly ascertained to exist.

### PROTOXIDE OF ZINC, ZnO; Eq. 40·6.

An ore of this oxide is known as red zinc ore. It is obtained by burning the metal in an earthenware crucible, as already described, or by throwing it down from its salts in form of hydrate by an alkali. Oxide of zinc forms colourless salts with acids; ammonia throws it down from these as potassa and soda do, and the precipitate is soluble in excess of ammonia. Its salts furnish a white sulphuret when treated by hydrosulphate of ammonia. The salts closely resemble those of magnesia. The oxide is now used extensively as a substitute for white lead, over which it possesses the advantage of not being apt to blacken by exposure to sulphuretted hydrogen.

### PEROXIDE OF ZINC

Is obtained by the action of oxygenated water on the hydrated oxide of zinc.

### CHLORIDE OF ZINC, ZnCl; Eq. 64·81;

Is formed when zinc in fine division is introduced into chlorine, when combustion takes place, or when the metal is dissolved in muriatic acid. It melts at 212°, is a very deliquescent salt, and is volatilised at a high temperature. This substance is used for preserving wood. As a disinfecting agent, it can only act on the solids or fluids with which it comes in contact, not on pernicious miasmata or floating poisons in the air. Iodide of zinc is like the chloride.

### SULPHATE OF ZINC, WHITE VITRIOL, $ZnO,SO_3+7HO$; Eq. 81·31+63

May be formed either by the oxidation of the sulphuret at a high temperature in contact with air, or by dissolving the oxide in sulphuric acid. The solution, on being evaporated, yields rhombic prismatic crystals, isomorphous with sulphate of magnesia. These are soluble in $2\frac{1}{2}$ parts of water at 60°, and undergo the watery fusion when heated.

The properties of the salts of zinc enable them readily to be distinguished.

Zinc alloys itself with copper to form the most useful compound of the metals—brass.

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### 34. CADMIUM, Cd.

Eq. 55·83; sp. gr. 8·6. In the process for reducing zinc, already described, cadmium comes over in the first part of the process, being more

volatile than zinc. If, therefore, in the process for preparing zinc, as cadmium is associated in small quantities with it in most of its ores, the process be conducted so as to preserve the first part of the products of distillation, and these are dissolved in an acid menstruum, the cadmium may be separated by means of sulphuretted hydrogen, which will throw down the yellow sulphuret of cadmium from such a solution. This sulphuret is to be dissolved in muriatic acid, 'when 'sulphuretted hydrogen is expelled, and a chloride formed; from this the carbonate is thrown down by excess of carbonate of ammonia. The carbonate is then ignited, and the 'metal reduced by distillation from carbon, on the same principle as zinc. The differences between this metal and zinc have been already stated. No very particular applications of cadmium have yet been made.

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## 35. COPPER, Cu.

Eq. 31·7. This metal is very generally diffused. It often occurs native crystallised in cubes and octohedrons. One of the commonest ores is a compound of sulphuret of copper and sulphuret of iron, known as copper pyrites. Here the copper occurs as a sulphuret, generally in combination with sesquisulphuret of iron, or with other sulphurets. In order to procure copper from these sulphurets, the ore, freed as much as possible from the impurities, is washed in a reverberatory furnace with siliceous matter. In this way the iron is converted into a fusible silicate; while the copper not being so easily oxidated, remains as a fusible subsulphuret. By this process, the copper then is left as a sulphuret, the iron becomes oxidated; the mass is run in a melted state into a cistern of water, and granulated.

The product is again washed and fused with ores containing oxide of copper, and the residue of other operations, which causes a double decomposition to take place with the remaining sulphuret of iron, oxide of iron and sulphuret of copper being formed, and the oxide of iron combining with more silicate, so as to form a slag. A subsulphuret of copper remains, nearly free of other metals. This is again submitted to a fresh roasting and reduction by carbon in contact with silica, by which more and more of the iron, and other oxidable substances, are separated; and, in conclusion, a strong blast of air is directed on the surface of the melted copper, which is stirred with a pole of green wood, in order that gases possessed of great reducing powers may be disengaged.

Cast copper has a sp. gr. of 8·83; hammered copper of 8·95. In fusibility it stands between silver and gold. Weak acids do not act upon copper, unless with the assistance of the air. For instance, vinegar does not affect copper, unless in much the same way as iron is rusted from the joint action of air and moisture. Unlike zinc, copper hardly dissolves in an acid by substitution for hydrogen. This is what we might expect from the use of copper in relation to zinc in the

galvanic arrangement. Copper is most powerfully acted upon by nitric acid. Copper forms three compounds with oxygen—the sub-oxide, $Cu_2O$; the protoxide, $CuO$; and the binoxide, $CuO_2$.

### SUBOXIDE OF COPPER, *Red Oxide,* $Cu_2O$; Eq. 71·42.

This compound occurs native, and may be prepared by heating to redness five parts of the protoxide and four of copper clippings in a covered crucible. This oxide is also formed when salts of the protoxide are partially reduced by some organic substances. It is a brown powder; and as it is not further changed in the air, the surfaces of copper vessels are often covered with it,—bronzed, to resist the action of the air. This may be done by covering them with a composition containing peroxide of iron, heating, and then cleaning the surface. The suboxide of copper is soluble in liquor-ammonia, form-ing a beautiful blue solution. Suboxide of copper is a very feeble base. In general, when weak acids act on it, they dissolve the pro-toxide, leaving metallic copper, and forming a salt of the protoxide. Thus $2Cu_2O + SO_3 = CuO,SO_3 + Cu$. Strong muriatic acid dissolves it, and forms a subchloride. Suboxide of copper colours glass of a beautiful red; but if it absorbs oxygen in the process, the glass is green.

### PROTOXIDE OF COPPER, *Black Oxide of Copper,* $CuO$; Eq. 39·51.

When copper is oxidated by the action of heat and air, this oxide is formed; but its ordinary mode of preparation is by igniting the nitrate. The nitric acid is driven off, and oxygen remains. This oxide, which is perfectly black, is possessed of pro-perties of the greatest value in organic analysis. It readily yields its oxygen when heated with organic substances containing carbon and hydrogen—converting the former into carbonic acid, and the latter into water. This oxide readily dissolves in acids. Its oxide is precipitated as a hydrate by decomposing a solution of a salt of copper with excess of caustic potass. This same hydrate is thrown down by ammonia, and then re-dissolved in excess of ammonia, forming a beautiful blue solution.

The binoxide of copper has been obtained by the action of oxy-genated water on the protoxide.

### CHLORIDES OF COPPER.

SUBCHLORIDE, $Cu_2Cl$; Eq.98·9.—May be obtained in several ways. One consists in heating copper filings with twice their weight of corro-sive sublimate.

CHLORIDE OF COPPER, $CuCl$. Eq. 67·2.—Obtained by dissolving the black oxide in muriatic acid. The solution may be crystallised in blue prisms, which contain 2 eq. of water.

The SUBIODIDE OF COPPER, $Cu_2I$—Is thrown down as a white precipitate when a solution of one part of sulphate of copper and 24 parts of protosulphate of iron are treated with a solution of iodide of potassium.

## SULPHURETS OF COPPER.

SUBSULPHURET OF COPPER, $Cu_2S$—Occurs native as copper glance. It may be prepared by heating copper-filings with half their weight of sulphur.

SULPHURET OF COPPER, $CuS$, Eq. 47·7—Is formed when a soluble protosalt of copper is decomposed either by sulphuretted hydrogen or an alkaline sulphuret. It is a black powder, which, when heated in close vessels, gives off sulphur, and becomes $Cu_2S$, or, when exposed to the action of air and water, becomes oxidated, and forms the sulphate.

## SALTS OF THE OXIDE OF COPPER.

*Carbonate of Protoxide of Copper*—Occurs native in several forms. *Mysorine* is a neutral carbonate, malachite a bibasic carbonate, with 2 eqs. $CuO$, to one of carbonic acid and one of water ; and a sesqui-basic carbonate also exists native in various forms. When a solution of salt of protoxide of copper is decomposed by an alkaline carbonate, the bibasic carbonate is thrown down.

*Sulphate of Protoxide of Copper*, $CuO,SO_3HO+4HO$; Eq. 79·88+ 45—May be prepared in the laboratory by boiling copper with sulphuric acid, diluted with half its weight of water. Sulphurous acid is disengaged, the copper oxidated at the expense of one portion of $SO_3$, while another portion combines with the oxide formed. From the solution thus formed the sulphate crystallises in beautiful blue rhombic prismatic crystals, which have the above formula. Exposed to air, these crystals lose 2 eqs. of water, and lose their transparency. At 212° they lose the 4 eqs. of water, and form a light-blue powder. Sulphate of copper is soluble in 4 parts of cold, and 2 of boiling water. When exposed to a current of ammonia it absorbs it, forming a compound of 2 eqs. of sulphate of copper and 5 of ammonia. Several subsulphates of copper have been obtained. One of the most definite, having the formula $3CuO,SO_3+3HO$, is obtained by digesting the hydrated oxide in a solution of the sulphate. When sulphate of copper is treated with liquor ammoniæ, and the precipitate formed re-dissolved in excess of ammonia, a salt is formed which is a compound of sulphate of copper and ammonia, and the formula of which is $CuO,SO_3+NH_3,HO$. When sulphate of copper is triturated with carbonate of ammonia, a similar compound appears to be formed, the carbonic acid escaping with effervescence ; and also when ammoniacal gas is passed into a saturated hot solution of sulphate of copper, as long as the gas is absorbed, the salt can be obtained then in beautiful deep-coloured crystals.

*Nitrate of Copper*, $CuO,NO_5+3HO$—Crystallises from the solution of copper in nitric acid (see nitric oxide), in prismatic crystals, con-

taining 3 eqs. of water; or sometimes in rhomboidal plates, containing 6 eqs. Ammoniacal salts may be obtained with it as with the sulphate.

*Acetates of Copper.*—There are several. The *Neutral Acetate*, $CuO,C_4H_3O_3+HO$, is procured by dissolving the black oxide in acetic acid. It crystallises from the solution. Verdigris is a subacetate of copper, which is formed by the action of dilute acetic acid derived from various sources, sometimes from the residue of grapes, after the juice has been expressed. Ordinary verdigris is often a mixture of subacetate and carbonate.

### TESTS FOR COPPER.

Copper in solution may be recognised by the following tests:— 1st, the addition of ammonia, which gives a beautiful deep amethystine blue; 2nd, by the ferrocyanide of potassium, which gives a brown precipitate; 3rd, by the action of hydrosulphuric acid, which throws down a black precipitate from its salts; 4th, by the effect of metallic iron or tin, which decomposes its salts, throwing down metallic copper on the metal employed.

## 36. LEAD, Pb.

Eq. 103·56; sp. gr. 11·445. This metal occurs native in many forms, but it is almost invariably obtained from lead pyrites, or galena, a sulphuret of lead. From this it may be obtained by roasting with iron. This ore, freed from impurities as much as possible, is roasted with carbonaceous materials in a reverberatory furnace, and exposed to a strong current of air. The sulphuret is in this way partly brought into the state of sulphate, partly into that of oxide. And both sulphate and oxide are capable of affording oxygen by a continuation of the process to the sulphuret, and thus sulphurous acid being disengaged, the metal will be reduced. The materials present with the lead, as lime and quartz, form a slag, to which, at a particular stage of the process, the temperature being lowered, more lime is added, so that the slag may become more solid, and allow the lead to be run out of the furnace.

The process of refining lead, and separating the silver which it contains, affords a beautiful illustration of the application of science to the arts. Formerly lead was separated from silver by the process of cupellation, which consists in burning off the lead in a current of hot air, in the form of litharge. Now, as this litharge often requires to be again reduced to the form of lead, a great saving was effected by diminishing the quantity of lead which required to be cupellated. This was done from the discovery of a property of the alloy of lead and silver, little to be expected from *a priori* considerations. When such an alloy, on being melted, is allowed to cool, the lead crystallises out first; consequently, when lead containing silver, say to the extent of 20 ounces in the ton, is melted in an iron pot, and the crystals which form

in cooling are removed by a perforated ladle, the lead removed will contain less silver than what is left behind, so that at last what remains will contain perhaps 40 ounces to the ton. To both the portions the same processes of condensation are applied, so that at last the whole lead comes to be divided into two portions, the one containing perhaps 200 ounces to the ton, and the other almost free from silver, and much improved in many qualities by the process;—only the former is cupellated.

Lead has very little ductility; it melts at 612°, and contracts on cooling very considerably. It crystallises in octahedrons. When exposed to air and moisture, lead rapidly tarnishes, and the crust of oxide which forms, protects the rest of the metal from further action, unless it is exposed to the continuous action of water, which dissolves the oxide. Although only a 1-12,000th part of oxide is thus taken up, it is sufficient to render *soft* waters kept in lead cisterns, or passed through lead pipes, highly deleterious; but the presence of salts to any extent in water, and especially of carbonates and sulphates, causes salts of lead to be formed, on which the water has no further action. Hence perfectly pure water would be the most dangerous, if allowed to remain in lead cisterns.

Lead forms 3 distinct oxides—the Suboxide, $Pb_2O$; the Protoxide, $PbO$; and the Peroxide, $PbO_2$. It is not easily oxidated by acids.

### SUBOXIDE OF LEAD, $Pb_2O$;

Is a dark-grey powder, formed by heating the oxalate in close vessels to redness. The oxalate is obtained by the action of oxalic acid on a soluble salt of lead.

### PROTOXIDE OF LEAD, $PbO$; Eq. 111·56;

Is obtained by exposing lead at a high temperature to the action of a current of air; the yellow protoxide is then formed, and can be removed by skimming from the surface of the melted metal. The formation of this may be readily shown, by decomposing some sugar of lead, by heat, in a crucible. This substance is called *massicot ;* melted by a stronger heat, it forms a brick-red mass, composed of crystalline scales, which is called *litharge.* Perhaps the pure protoxide is best prepared by igniting the nitrate, and may be precipitated as a white hydrate from its soluble salts by means of potassa. All its salts are acted upon by sulphuretted hydrogen—even the sulphate. Zinc and iron remove the metallic lead from these salts in solution.

### PEROXIDE OF LEAD, $PbO_2$;

May be prepared in the same way as the peroxides of cobalt and nickel. It is of a dark-brown colour. It forms no salts.

*Minium,* or red lead, is a mixed oxide, prepared by exposing massicot to low redness in a peculiarly shaped furnace, and urging it with a current of air. Its composition is variable, but that generally given is $2PbO + PbO_2$. When minium is treated by strong acids, it

is resolved into the protoxide, which forms a salt with the acid, and peroxide, which remains behind.

### CHLORIDE OF LEAD, $PbCl$; Eq. $139 \cdot 16$;

Is easiest obtained by digesting oxide of lead in muriatic acid, or by precipitating a pretty strong solution of a salt of lead by an alkaline chloride. This compound is soluble in 135 parts of cold water. It crystallises from its hot solution in needles. It is an exceedingly fusible body.

### IODIDE OF LEAD, $PbI$; Eq. $229 \cdot 92$;

Is thrown down in the form of a beautiful yellow powder, when solution of iodide of potassium is added to a soluble salt of lead. It is a much more insoluble salt than the chloride.

### SULPHURET OF LEAD, $PbS$; Eq. $119 \cdot 56$;

Is thrown down as a black powder whenever sulphuretted hydrogen is passed through a solution of a salt of lead ; but the precipitate thus obtained, when *heated* in acid solutions, is readily dissolved, with escape of sulphuretted hydrogen gas. It is in this form that lead exists in galena.

*Carbonate of Lead—Ceruse, or White Lead* — $PbO,CO_2$, Eq. $133 \cdot 56$—occurs native ; may be formed by adding an alkaline carbonate to a solution of acetate of lead. When precipitated in this way from solutions, it has a crystalline structure, which renders it unfit for the purpose of a pigment, for which it is generally manufactured. It is generally prepared by what is termed the Dutch method. For this purpose it is first cast into pieces, of a form which will allow the air to pass through them, something like a gridiron, and these are placed over earthenware vessels containing weak acetic acid, which are imbedded in fermenting tan. The quantity of vinegar required is so small, as to show that the lead is not oxidated by it. The oxygen must come from the air, and the carbonic acid from the tan.*

*Sulphate of Lead*, $PbO,SO_3$.—This salt is formed when a soluble salt of lead is treated with sulphuric acid, or an alkaline sulphate.

*Nitrate of Lead*, $PbO,No_5$.—Prepared by dissolving litharge, with the aid of heat, in nitric acid. The solution concentrated yields white octahedral crystals. By boiling this nitrate with metallic lead, brilliant yellow crystals of *nitrite of lead* may be obtained.

*Acetate of Lead*, $PbO$, $C_4H_3O_3+3HO$, is prepared by dissolving litharge in acetic acid. It crystallises in four-sided prisms, which are remarkable for their sweetish, slightly-astringent taste. They are

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* Many attempts have been made to substitute other processes for the old Dutch mode of preparing white lead, and many to substitute other compounds of lead for it as a pigment, but hitherto with dubious success. The sulphate, the oxychloride prepared by the action of supercarbonate of magnesia or chloride of lead, have been proposed, and lately the arsenite, for some specific purposes.

soluble in less than twice their weight of water at 60°. When oxide of lead is boiled in solution of the acetate, a bibasic acetate is formed, and other basic acetates may be formed.*

### TESTS FOR LEAD.

These are very numerous. The following may be enumerated :—
1st. The action of iron and zinc on the solutions of lead, whereby beautiful crystalline plates of metallic lead may be formed on pieces of these metals, suspended for some time in solutions of salts of lead. 2nd. The action of sulphuretted hydrogen on all salts of lead. 3rd. The formation of a yellow precipitate when solution of iodide of potassium is added to these salts. 4th. The formation of a similar precipitate with red chromate of potass.

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## 37. BISMUTH, Bi.

Eq. 70·95; sp. gr. 9·53. Bismuth generally occurs native, and may be separated from the ores in which it exists by simple fusion.† Bismuth is a white crystalline metal, which melts at about 500°. It is volatilised at a red heat, and burns with a bluish flame, and formation of fumes of oxide of bismuth. It is not acted on by air, but dissolves readily in acids, in muriatic acid with evolution of hydrogen, and in nitric with evolution of compounds of nitrogen and oxygen. It has 3 oxides—a suboxide and a peroxide of little importance, and the

### PROTOXIDE OF BISMUTH, BiO ; Eq. 78.95 ;

Which is formed when the metal is burnt in the air, or by igniting the nitrate. It is a yellow powder, and is the basis of the salts of bismuth.

The most important salt of bismuth is the nitrate $BiO,NO_5 + 3HO$ ; eq. 133·33 + 27 ; it is obtained by the action of nitric acid, sp. gr. 1·42, on bismuth. The metal is dissolved with great rapidity, and on the solution being allowed to cool, crystals are obtained. These are four-sided prisms isomorphous with the analogous nitrate of magnesia. They are highly deliquescent. When thrown into water they are decomposed, and a compound, formed of three equivalents of oxide of bismuth with one of nitrate of water—that is to say, two equivalents of acid and water are removed from three of the neutral nitrate, and by long-continued washing all the nitric acid can be removed. The suboxide formed in

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* Lead forms several alloys, principally with tin. These are the solders most in use.—Fine solder is 2 of tin and 1 of lead; it melts at 360°. Coarse solder contains ¼th of tin, and melts at 500°.

† Pure bismuth is obtained by igniting the nitrate, and reducing the oxide thus obtained with charcoal. Its equivalent by many is trebled. This will depend a good deal on whether we choose to rank it in the class with zinc or antimony. Here it is made to rank with zinc, and the eq. 70·95 retained.

this way is that used in medicine, and called also the trisnitrate. Under the name of flake white it has been used as a cosmetic.

The chief uses of bismuth are in forming alloys. These are very fusible. Eight parts of bismuth, five of lead, and three of tin, form a substance known as Newton's fusible alloy, which melts at 203°, and is employed in taking moulds. Bismuth, owing to its property of expanding when cooling, is also used in the metal for types, which is thus caused to take the finest impressions when cast into the type moulds.

Bismuth may be recognised by the action of sulphuretted hydrogen on its salts giving rise to a black precipitate; by the action of water in decomposing most of them; by yellow prussiate of potass giving a white precipitate with them; and by its oxide fusing before the blow-pipe, being dark-brown when hot, yellow when cooled, and being reduced on charcoal, and giving a colourless bead when fused with borax.

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Sect. 5.—Other Metals, having Isomorphous Relations with the Magnesian Family, but differing in many respects from the preceding class, so that they are put into a separate class.—These are, Tin, Titanium, Chromium, Vanadium, Tungsten, Molybdenum, Tellurium.

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### 38. TIN, Sn (Stannum).

Eq. 58·82; sp. gr. 7·28. Tin occurs in nature chiefly in the form of the deutoxide, which is generally associated with other metals, and especially with arsenic. It is found in two forms in Cornwall—either in veins traversing the primary rocks, where it is more apt to be associated with other metals, or in rounded grains which have been exposed to the action of water, and deposited in beds of clay or gravel. The latter is called stream tin, and is much the purer form. The metal is obtained chiefly by roasting the ore with charcoal or coal, and then fusing it at a certain temperature, and stirring it repeatedly; the greater part of the impurities are driven off by the former process, and, in the latter, their separation completed, by the greater fusibility of the tin. Tin melts at 442°; on cooling, it crystallises; like most metals, it assumes the octahedral form, but the usual crystals are prisms. Owing to this crystalline character, when a bar of tin is bent it crackles. Tin is hardly volatile. It is little liable to oxidate in the air, a circumstance to which many of its most valuable properties are owing. It is very malleable, but has little tenacity. When melted in air, it is covered with a film of oxide, and, at a white heat, it burns. Nitric acid pure does not act on tin, but, if a little diluted, a violent action takes place, compounds of

oxygen and azote, with some ammonia are disengaged, and metastannic acid, $Sn_5O_{10}$, formed. Muriatic acid readily dissolves tin; sulphuric acid more slowly.

Tin forms several compounds with oxygen, of which the more definite are, the Protoxide, $SnO$; the Deutoxide or Binoxide, $SnO_2$; and the compound already named Metastannic Acid.

### Protoxide of Tin, $SnO$; Eq. 66·82;

Is obtained by the action of solution of an alkaline carbonate on solution of chloride of tin. There is no carbonate precipitated, but a white hydrate of the protoxide, which may be washed and dried at a temperature below 176°. Dried and heated in an atmosphere of carbonic acid, it yields the anhydrous oxide in the form of a black powder. This oxide may be obtained in different forms by various processes, furnishing thus a good illustration of allotropy. For instance, if the solution of chloride of tin be decomposed by potassa instead of the carbonate, and the precipitate redissolved by excess of the alkali, and the whole evaporated in vacuo (see potassa, fig. 26), then black crystals of the oxide are formed, and, by a somewhat similar process with ammonia, a red oxide may be obtained. When oxide of tin is heated in the air it burns with great facility, and is converted into the deutoxide.

### Deutoxide of Tin, $SnO_2$; Eq. 74·82;

Termed also stannic acid. Stannic acid is prepared as a hydrate by precipitating a solution of bichloride of tin with a solution of an alkaline carbonate. The precipitate should be well washed. When this precipitate is dried in *vacuo*, it forms gummy-like masses, in which one eq. of water is combined with one of the peroxide. The peroxide in this state is quite soluble in muriatic acid; but if it is digested for some time in boiling water, it is then found only to be very partially soluble in muriatic acid. It may also be obtained by throwing the bichloride of tin into water. This body can be made to form compounds called *stannates* with alkalies, and it even forms a *stannate* with the protoxide itself, which is also as a base termed a sesquioxide.

### Metastannic Acid, $Sn_5O_{10},10HO$;

Is obtained when tin is acted on by nitric acid. It is a crystalline powder, which is found to contain 10 eq. of water. Dissolved in potass it forms the metastannate of potass.

### Chloride of Tin (Protochloride), $SnCl+3HO$; Eq. 94·32+27;

May be prepared by distilling a mixture of equal parts of calomel and tin at a red heat. It may also be obtained in the form of hydrate by dissolving tin in muriatic acid, diluted with an equal weight of water. A portion of the metal is left undissolved, and, on evaporating the solution, acicular crystals are obtained. This salt dissolves readily

in water, but is decomposed by a large quantity of this fluid in something of the same way that the salts of bismuth are decomposed, a portion of chlorine being removed by the water in the form of muriatic acid, and the bismuth of that portion oxidised, so that an oxichloride is formed, $2SnCl + HO = SnCl,SnO + ClH$. This salt absorbs oxygen rapidly from the air, and when added to solutions of many metals, reduces them to the metallic state. It also absorbs colouring matters from their solutions, and hence is used as a mordant.

### BICHLORIDE OF TIN, $SnCl_2$; Eq. 129·82.

The anhydrous bichloride known as the fuming liquor of Libavius, may be obtained by distilling four parts of corrosive sublimate, mixed with one of tin-filings.* A colourless liquid is distilled over. It fumes in the air. When mixed with water it is solidified, forming a crystalline hydrate, in which two eq. of the bichloride are combined with five eq. of water.

### SULPHURETS OF TIN, $SnS$, $SnS_2$.

The protosulphuret may be obtained by the direct union of tin and sulphur, or by passing sulphuretted hydrogen through a solution of a protosalt of tin; the black sulphuret is precipitated. The bisulphuret is called mosaic gold, and is used for the coarser kinds of gilding. For this purpose it must be prepared in the *dry way*. This is done by heating in a covered crucible a mixture of twelve parts of tin, seven of sulphur, and six of muriate of ammonia. When thus prepared it is in bright yellow scales. When thrown down from solutions of the persalts of tin by sulphuretted hydrogen, this substance is of a dirty yellow colour.

The salts of the oxide of tin are of little moment. The salts of tin may be recognised thus,—those of the protoxide, by their giving metallic tin when heated, by the effect of sulphuretted hydrogen, and prussiate of potass giving a white precipitate. Those of the peroxide give the precipitate described with sulphuretted hydrogen, and a yellow precipitate with prussiate of potass.

Tin forms alloys of great value. With antimony, copper, and bismuth it forms pewter. In the state of foil, it is used for preserving many substances from the air; and for this purpose also it is employed to cover iron, forming the substance generally known as tin-plate. It is also used, amalgamated with mercury, to silver looking-glasses, and forms, besides, a variety of useful alloys.

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## 39. TITANIUM, Ti.

Eq. 24·29; sp. gr. 5·3; Is found in nature in several minerals, rutile, anatase, &c., almost pure, except that it is not native, but

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* It may also be obtained by the direct union of chlorine and tin, as by passing a stream of chlorine over tin-foil or granular tin.

combined with oxygen, or in ores combined with iron. It is obtained by reducing titanic acid with charcoal, by the highest heat of a wind furnace, or such a blast furnace as in fig. 31. Titanium is a dark-green powder, infusible, which, when heated in air, burns, and forms titanic acid. Acids do not act upon titanium, except a mixture of hydrofluoric and nitric acids. It forms three oxides—a Protoxide, TiO ; a Sesquioxide, $Ti_2O_3$ ; and a Peroxide, termed titanic acid, $TiO_2$.

### PROTOXIDE OF TITANIUM, TiO ;

Is produced when titanic acid is heated intensely in a crucible lined with charcoal; the acid near the charcoal is reduced to the metallic state; but that in the centre of the masses is changed into the oxide. It is a black substance. It is also formed by heating titanic acid with potassium. It is scarcely soluble in acids and alkalies.

### SESQUIOXIDE OF TITANIUM, $Ti_2O_3$ ;

Is obtained by passing a current of hydrogen over titanic acid strongly heated. It may also be obtained by the action of an alkali on the sesquichloride. It rapidly absorbs oxygen, and becomes titanic acid.

### TITANIC ACID, $TiO_2$ ; Eq. 40·29 ;

Is the form in which titanium exists native. It is obtained by heating rutile with chloride of barium. By this, after the mass has been freed by washing from excess of chloride of barium, a titanate of baryta and peroxide of iron are obtained. By the action of sulphuric acid and water, titanic acid and sulphate of iron are obtained in solution, and sulphate of baryta left behind; sulphuretted hydrogen is passed through the solution to get rid of any tin which may exist; and then ammonia is added to neutralise the solution ; titanic acid is thrown down. It is digested with solution of sulphurous acid, to free it from any sulphuret of iron, and then the titanic acid washed remains pure. Titanic acid is a white powder, infusible and insoluble in water. When previously heated with an alkaline carbonate, it becomes soluble in muriatic acid. The solution gives a yellow colour with infusion of galls, characteristic of this acid. When this solution is neutralised by ammonia, a gelatinous precipitate is thrown down, which is this soluble titanic acid. On this being collected, dried, and heated, it becomes incandescent, and loses its property of solubility.

### CHLORIDES OF TITANIUM.

A Sesquichloride and a Bichloride are known.

### SESQUICHLORIDE OF TITANIUM, $Ti_2Cl_3$ ;

Is obtained by passing through a tube heated to redness, vapour of hydrogen, which has been made to absorb bichloride of titanium at a red heat; crystals of the sesquichloride form in the cool part of the tube. The effect of the hydrogen is to deprive the bichloride of a

portion of its chlorine. The sesquichloride is found thus prepared in violet scales, and presents very remarkable desiccating properties.

## BICHLORIDE OF TITANIUM, $TiCl_2$;

Is produced by passing chlorine over metallic titanium at a red heat. It is a colourless liquid, and boils at the same temperature as water.

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## 40. CHROMIUM, Cr.

Eq. 28·15.; sp. gr. 5·9. This metal exists native in several minerals, amongst which may be particularly mentioned the chromates of lead and chrome-iron. The latter substance is an ore of the composition $FeO + Cr_2O_3$. When this ore is calcined with carbonate of potass, with or without some nitrate, in a reverberatory furnace, the oxide of chromium, by absorption of oxygen, is converted into chromic acid, which combines with the potass forming chromate of potass. At the same time the iron is peroxidised. By lixiviating the mass, a mixture of carbonate and chromate of potass is obtained. The addition of sulphuric acid gives rise to a bichromate and a sulphate. As this former salt is much the more soluble, the two can be separated by crystallisation. Metallic chromium is obtained by reducing the oxide in a crucible lined with charcoal, in a blast furnace. It is of a greyish-white colour, very infusible. It is not oxidated in the atmosphere at ordinary temperature. Acids act upon it with difficulty, but, heated with alkalies, it forms chromic acid. It forms four compounds with oxygen— the Oxide, or Protoxide, CrO; the Sesquioxide, $Cr_2O_3$; Chromic Acid, $CrO_3$; and Perchromic Acid, $Cr_2O_7$. The existence of the first is doubtful, or at least it is soon resolved into a mixture of oxide and sesquioxide by absorption of oxygen.

## SESQUIOXIDE OF CHROMIUM, $Cr_2O_3$; Eq. 80·30;

Is obtained by igniting the chromate of mercury; in the first place, solution of chromate of potass and nitrate of mercury are mixed, and the precipitate which forms is then ignited. It is thus obtained as a green powder; but it may be procured in the form of very dark-green crystals, by passing the vapour of chlorochromic acid through a tube heated to an intense heat. The chlorochromic acid (see its formula) is decomposed, and oxide of chromium forms in the cooler portion of the apparatus. In these forms it is not soluble in acids. It may be obtained as a hydrate soluble in acids, by adding hydrochloric acid and alcohol alternately to a boiling solution of bichromate of potass.

This substance is very useful in colouring stone-ware pink.

## CHROMIC ACID, $CrO_3$; Eq. 52·15;

May be obtained by passing fluosilicic acid, prepared by heating in a glass retort, fluor spar, sulphuric acid and glass, into a hot solution

of bichromate of potass.* The potass is removed by the formation of a fluosilicate of potassa, or fluoride of silicon and potassium, which is insoluble. The solution, evaporated to dryness, gives a residuum, which is to be redissolved for use. It forms a yellow solution. This acid is a very powerful oxygenating agent, bleaches like chlorine, and, in doing so, is reduced to the state of sesquioxide. It combines with several bases, and possesses considerable chemical power. Its salts are distinguished by their splendid colours. The solution exposed to the light loses a portion of its oxygen, and the sesquioxide formed combines with another eq. of chromic acid, and forms a chromate of that base.

SALTS OF CHROMIC ACID. The *Chromate of potass* is prepared by the addition of carbonate of potass to a solution of the bichromate, which latter is obtained, as described, from chrome ore. It crystallises in double pyramids of six faces, or in oblique four-sided prisms, isomorphous with the sulphate. These are of a beautiful yellow colour. The *bichromate* crystallises in fine red tables. The *chromate of lead*, known as chrome yellow, a fine yellow salt, is obtained by the reaction of salts of lead and chromates of potass. The *subchromate of lead* is obtained when an equivalent of chromate of potass, one of free potassa, and one of nitrate of lead, meet together; the equivalent of alkali retains half an equivalent of the chromic acid. Chromate and nitrate of potass can be removed by washing, and the red subchromate remains. All these salts are much used in dyeing, and as pigments.

### PERCHROMIC ACID, $Cr_2O_7$;

Is a very unstable acid, and soon passes into the sesquioxide by loss of oxygen. It may be formed by the action of oxygenated water on the former compound.

### CHLORIDE OF CHROMIUM, $Cr_2Cl$.

Obtained by heating sesquioxide in a current of chlorine. It rapidly absorbs oxygen from the air, and forms an oxychloride.

### SESQUICHLORIDE OF CHROMIUM, $Cr_2Cl_3$.

A solution of this substance may be procured by dissolving the hydrate of the sesquioxide in muriatic acid. It is of a fine green colour.

### CHLOROCHROMIC ACID, $CrCl_3$, $2Cr_2O_3$;

May be obtained by distilling in an ordinary retort 3 parts of bichromate of potass, and $3\frac{1}{2}$ parts of the muriate of soda, triturated

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* Equal parts of pounded fluor spar, and glass, with six parts of strong sulphuric acid, are to be used. For the theory of the process see Fluorine. The fluorilic acid is to be passed into the solution as long as any potass remains, which can be ascertained by testing.

together along with 5 by measure of sulphuric acid. A red liquid will be found in the receiver. This also is a powerful oxidating agent. Water resolves it into chromic and muriatic acids.

The compounds of chromium are easily recognised by their striking reactions.

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## 41. VANADIUM, V.

Eq. 68·55. A very rare metal, which has been found associated with iron and lead. In its general properties, it bears some relation to chromium. It forms three compounds—the protoxide, $VO$; the binoxide, $VO_2$; and the teroxide, $VO_3$, which has acid properties, and is called vanadic acid. The salts are formed by the second compound. The vanadic acid, from which the other oxides are formed, may be prepared by dissolving the natural vanadiate of lead in nitric acid, precipitating lead and arsenic by sulphuretted hydrogen; there is then a blue solution of binoxide of vanadium, which, on being evaporated to dryness, forms vanadic acid. Vanadic and chromic acids both form red solutions; but the former becomes blue, and the latter green, when they are deoxidised.

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## 42. TUNGSTEN, W.

Eq. 94·64; sp. gr. 17·6. Exists chiefly in the mineral called wolfram, where it is in the form of tungstic acid. The metal is prepared from the tungstic acid by the reducing action of hydrogen at a high temperature, or in the way in which manganese and similar metals are reduced by charcoal. It is a dark-grey, almost infusible metal. In specific gravity it is next to gold and platinum. As it is obtained by reduction with hydrogen, it is in the spongy form, and takes fire in air, being converted into tungstic acid. It forms two compounds with oxygen—the tungstic oxide, $WO_2$; and the tungstic acid, $WO_3$. The former is prepared when the latter is exposed to a current of hydrogen at a low red heat. The latter is obtained from wolfram by simply acting on the ore with aqua regia, which dissolves out the iron and manganese. The residue, after being washed, is dissolved in ammonia, whereby a tungstate of ammonia is formed; and the solution evaporated and ignited leaves tungstic acid. Tungstic acid is a yellow solid, which by heat loses a portion of its oxygen, and is converted into a compound with the oxide. This is of a blue colour. Tungstates are readily formed with alkalies, as may be seen, from the action of ammonia; but the acid is perfectly insoluble in water and acids. Tungsten forms compounds with chlorine sulphur, &c.

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## 43. MOLYBDENUM, Mo.

Eq. 47·88; sp. gr. 8·52. This is a very rare metal, in many respects closely resembling tungsten, but differing, as will be seen, greatly in weight. It occurs in nature in the form of a sulphuret, closely resembling plumbago, or in the form of molybdate of lead. It may be prepared from molybdic acid by processes precisely analogous to those for tungsten. It is a white metal, which is not acted on by dilute acids, but soluble in aqua regia, nitric acid, or strong sulphuric acid. It forms three oxides — the protoxide, MoO; the binoxide, $MoO_2$; and the teroxide, termed molybdic acid, $MoO_3$. The first is best prepared by dissolving one of the salts of the acid in hydrochloric acid, and introducing a piece of zinc. The solution undergoes several changes of colour; and chloride of zinc and protochloride of molybdenum are formed. Ammonia is then added carefully to the fluid, so as to throw down the oxide of molybdenum, and leave the zinc, some oxide of zinc carried down is removed by repeated washing with ammonia, when the black hydrate of the oxide of molybdenum remains. It is scarcely soluble in acids. The binoxide may be obtained mixed with a little protoxide, by igniting the molybdate of ammonia in a covered crucible. Prepared in this mode, it is insoluble in acids. It may be procured hydrated by dissolving molybdic acid and copper in muriatic acid, and adding excess of ammonia, which precipitates the binoxide, and leaves the copper in solution. This hydrate forms salts with acids, which are red when hydrated, and crystallised and black when anhydrous. The molybdic acid is obtained by roasting the native sulphuret, dissolving the residue in ammonia, and then crystallising and igniting the crystals of molybdate of ammonia. It is left as a porous substance, which melts at a red heat, and then assumes a crystalline structure on cooling, and is of a yellow colour. Its salts are colourless, when the base is so. They are readily formed. When molybdenum is heated in an atmosphere of chlorine, it forms a dark-red gas, which is deposited in crystals like iodine, analogous to the chlorochromic acid.

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## 44. TELLURIUM, Te.

Eq. 66·14; sp. gr. 6·25. This is another rare metal, found in conjunction with gold, silver, lead, and bismuth, which presents several analogies with sulphur. Tellurium may be obtained from the tellurite of bismuth, by heating it with carbon and carbonate of potass. In this process, metallic bismuth and a tellurite of potassium is formed. The latter is soluble, and from the solution tellurium is gradually deposited. Tellurium is a brilliant silvery metal. It can be crystallised in rhombohedral crystals, isomorphous with those of arsenic and antimony. It melts at

about 800°, and volatilises at a higher temperature. It burns when heated in the air, forming tellurous acid, $TeO_2$. The same acid may also be obtained by other processes, as by decomposing bichloride of tellurium by cold water. It is a white earth-like substance, generally crystalline, readily soluble in acids and in alkalies, with which it forms tellurites. The telluric acid, $TeO_3$ may be prepared first by fusing tellurous acid with nitre, and thus forming a tellurate of potash, which may be decomposed by hydrate of baryta, and the insoluble tellurate of baryta by sulphuric acid. It may be crystallised from its solutions along with 3 eqs. of water. The bichloride of tellurium may be prepared by heating tellurium in chlorine. Telluretted hydrogen, a gas similar to sulphuretted hydrogen, is obtained by fusing tellurium with tin or zinc, and treating the result with muriatic acid. Sulphuretted hydrogen gives a brown precipitate with the salts of tellurous acid, and a black with those of telluric acid; alkalies and alkaline carbonates a white precipitate with the tellurites, soluble in excess of the reagent.

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Sect. 6.—Metals Isomorphous with Phosphorus.—These include Arsenic, Antimony, and Bismuth.*

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## 45. ARSENIC, As.

Eq. 75; sp. gr. 5·75. Arsenic occurs native—mostly along with other metals; generally it is found as a sulphuret in combination with other metals, as iron, cobalt, and nickel. It is generally obtained by roasting the sulphuret with the addition of iron, which retains all the sulphur, while the arsenic is oxidated and sublimed in the form of arsenious acid. To obtain metallic arsenic, the arsenious acid is mixed with twice its weight of black flux,† and heated in a crucible, within which another crucible is inserted and inverted. The crucibles are luted together, and a little hole is made in the upper, or, better still, a bent tube connected with the upper part. The upper crucible should be kept cool. The arsenic sublimes into the upper crucible. A little can readily be made in a glass tube or retort. Arsenic crystallises in rhombohedrons. It is a very brittle metal. It sublimes at 360° without

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* Bismuth has already been treated of, on account of its resemblance to lead.

† Black flux is prepared by igniting cream of tartar, or bitartrate of potass. It is the same substance as is used in preparing potassium. Its carbonate of potass takes the sulphur, and its carbon prevents, or helps to prevent, the oxidation of the arsenic.

previously melting. It has a smell like garlic, and forms two compounds with oxygen—$AsO_3$, or arsenious acid; and $AsO_5$, arsenic acid.

## ARSENIOUS ACID, $AsO_3$; Eq. 99 (Arsenic—White Arsenic);

Occurs in two forms, as obtained by sublimation, and as sold in commerce unground. Some is opaque and quite white; another kind of a more vitreous character, yellowish and translucent. These varieties differ in density, the latter being 3·738, the former 3·369. The opaque kind is also more soluble—100 parts of water at 212° dissolving 11·47 of it, while they only dissolve 9·68 of the vitreous; and when the solutions cool to 60°, 2·9 of the former remain in solution, and only 1·78 of the latter. Arsenic, therefore, is another instance of allotropy. Arsenious acid volatilises below a red heat. When arsenious acid is slowly sublimed in a glass tube, it crystallises in regular octahedrons. It occurs sometimes in prisms. Arsenious acid boiled with alkaline solutions combines with them. It also forms salts with metals, some of which are very definite.

## ARSENIC ACID, $AsO_5$; Eq. 115;

Is obtained by digesting arsenious acid with nitric acid, as long as red fumes are disengaged. The mass is then dried and heated to expel excess of nitric acid. It must not, however, be heated above 600°, for above that temperature it is resolved into arsenious acid and oxygen. Arsenic acid is a white solid, which deliquesces when exposed to the air. Arsenic acid is distinctly sour, while arsenious acid is not. When arsenic acid is heated with excess of carbonate of soda, it forms a tribasic arseniate isomorphous with the corresponding subphosphate, having a formula $3NaO,AsO_5+24HO$. By adding carbonate of soda to a hot solution of arsenic acid as long as carbonic acid is expelled, and then evaporating, a salt is obtained corresponding to the common phosphate of soda—*i. e.*, containing two of soda and one of basic water. Like common phosphate of soda, it sometimes has 14, sometimes 24 eqs. of water of crystallisation, forming $2NaO,HO,AsO_5+14HO$. This salt is more soluble than the phosphate. When to this salt an eq. of arsenic acid is added, a binarseniate is formed corresponding to the biphosphate. But those changes which take place on phosphoric acid itself cannot be imitated by arsenic acid; because, although these salts, like the phosphates, lose their water at a red heat, they recover it again when redissolved. Arsenic acid, therefore, only forms one class of salts. The alkaline arseniates are soluble; the metallic ones insoluble.

### CHLORIDES OF ARSENIC.

A subchloride is supposed to exist    The ordinary chloride corresponds to arsenious acid. It may be formed directly by introducing metallic arsenic into chlorine gas. The arsenic takes fire. It may also be obtained by distilling the metal with six parts of corrosive sublimate. A similar bromide and iodide may be formed.

## SULPHURETS OF ARSENIC.

Of these there are several; but the chief are, the tersulphuret, called also orpiment and sulpharsenious acid, having a formula of $AsS_3$, which is prepared by decomposing a solution of arsenic in muriatic acid by sulphuretted hydrogen, or an alkaline sulphuret. When heated it melts, and then sublimes. It combines with alkaline sulphurets as an acid, forming double salts. Heated with black flux it yields metallic arsenic. The sulpharsenic acid, or realgar, is formed when sulphuretted hydrogen is passed through arsenic acid. Its formula is $AsS_5$. It is very like orpiment, readily melts, and acquires a red colour, and sublimes at a low temperature; it is a more powerful sulphur acid than the former compound.

## ARSENIETTED HYDROGEN, $AsH_3$;

Is obtained from the mutual action of zinc and sulphuric acid. The arsenic combines with the hydrogen disengaged, and arsenietted hydrogen is obtained. Arsenietted hydrogen has a garlic smell, somewhat similar to that of metallic arsenic. Its sp. gr. is 2·69; it is soluble in water; when inflamed in air, the products of its combustion are arsenious acid and water. It is decomposed by chlorine with combustion.

Arsenic forms numerous alloys with metals. Its principal use this way is to harden tin.

### TESTS FOR ARSENIC.

The metal may be recognised by subliming it, and by its solution in hydrochloric acid, giving the characteristic results obtained with arsenious acid.

Arsenious acid is detected in two ways—first, by what are termed fluid tests, and also by what are called reduction tests. The principal fluid tests are—1st, The ammonio nitrate of silver, which gives a yellow precipitate with solutions of arsenious acid. The presence of ammonia enables the arsenious acid to take the place of the nitric, by the affinity of the ammonia for the latter—arsenite of silver and nitrate of ammonia being formed. 2nd, The ammonio sulphate of copper gives a green precipitate, called Scheele's green. 3rd, Sulphuretted hydrogen throws down a yellow precipitate. Although objections may be taken to these tests separately, yet if they all give these results, no objection applies to the inference from the three of the presence of arsenic, since there is no substance whatever which would give all these three results, but arsenic. If arsenious acid is in the solid form, it can be heated, when it will be sublimed in octahedral crystals, which may require to be examined with the miscroscope if the quantity be small; or it may be heated in a tube, when a sublimate of metallic arsenic will be obtained; or it can be boiled in water, and the fluid tests applied to the solution. The reduction tests are—1st, The obtaining

of the metal from the sulphuret in a tube, as in fig. 32, by heating it with black flux. 2nd, Marsh's test, which consists in acting upon the suspected solution with zinc and sulphuric acid, in an apparatus like that in fig. 33. Here the solution should *nearly* touch the cork to which the stopcock is attached; on turning the stopcock, if arsenic be present, arsenietted hydrogen will be evolved; on inflaming this, and holding a porcelain plate close to the hole of the jet attached to the stopcock, it will receive a fine hair-brown stain of metallic arsenic. If, however, it be held at a distance, an opaque white spot will be produced. A glass plate is more suitable for this experiment. What takes place is this—the hydrogen of the arsenietted hydrogen is the more combustible of its two elements, and it burns first, so that when the porcelain is placed close to the jet, the arsenic not having time or space to burn, is deposited in the metallic form; but further off it has burnt too, and in that position it is deposited as white arsenious acid. 3rd, What is termed Reinsch's test, when solutions containing arsenic are acidulated with muriatic acid and boiled with copper, a black metallic coat of arsenic is thrown down on the copper. On heating this copper in a moderately wide tube (see fig. 34), it loses its black colour, and a ring of white octahedral crystals is obtained.

To these tests various objections have been made. Other metals as well as arsenic are precipitated by boiling their solutions with copper and muriatic acid; but then they do not sublime from it in the form that arsenic does. Cadmium gives a yellow precipitate with sulphuretted hydrogen; but the sulphuret is insoluble in ammonia, in which the sulphuret of arsenic may be dissolved. Antimony forms an antimoniuretted hydrogen gas, analogous to the arseniuretted, and which burns too; but the stain of antimony is of a sooty black, totally unlike the fine brilliant hair-brown stain of arsenic. The sulphuric acid and zinc employed may contain arsenic; this is obviated by testing them in the Marsh's apparatus *before* the suspected fluid is introduced. The test most open to fallacy is that of the sulphate of copper; for several substances give precipitates more or less green with ammonio sulphate of copper, and organic matter does so.

The great difficulty in testing for arsenic is the presence of organic matter. If a solution containing organic matter be put into a Marsh's apparatus, the frothing is so great as to impede the action of the apparatus; if organic matter be present when Reinsch's test is tried, some of it is precipitated upon the copper, and if the quantity of arsenic be small, it will impede the distinct appearance in the sublimate of octahedral crystals, and in the test by sulphuretted hydrogen, it will impede the reduction of the arsenic as a bright metallic crust.

The getting rid of organic matter in the contents of the stomach, or tissues of the body, is the great difficulty in searching for evidence of the presence of arsenic. For this several methods have been invented, especially since the discovery of the great physiological fact, that arsenic, like many other poisons, is absorbed into all the tissues of the body, and may be recovered from them. One very good way, when the contents of the stomach are in question, and they are not

taining 3 eqs. of water; or sometimes in rhomboidal plates, containing 6 eqs. Ammoniacal salts may be obtained with it as with the sulphate.

*Acetates of Copper.*—There are several. The *Neutral Acetate,* $CuO,C_4H_3O_3+HO$, is procured by dissolving the black oxide in acetic acid. It crystallises from the solution. Verdigris is a subacetate of copper, which is formed by the action of dilute acetic acid derived from various sources, sometimes from the residue of grapes, after the juice has been expressed. Ordinary verdigris is often a mixture of subacetate and carbonate.

### TESTS FOR COPPER.

Copper in solution may be recognised by the following tests:— 1st, the addition of ammonia, which gives a beautiful deep amethystine blue; 2nd, by the ferrocyanide of potassium, which gives a brown precipitate; 3rd, by the action of hydrosulphuric acid, which throws down a black precipitate from its salts; 4th, by the effect of metallic iron or tin, which decomposes its salts, throwing down metallic copper on the metal employed.

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## 36.  LEAD, Pb.

Eq. 103·56; sp. gr. 11·445. This metal occurs native in many forms, but it is almost invariably obtained from lead pyrites, or galena, a sulphuret of lead. From this it may be obtained by roasting with iron. This ore, freed from impurities as much as possible, is roasted with carbonaceous materials in a reverberatory furnace, and exposed to a strong current of air. The sulphuret is in this way partly brought into the state of sulphate, partly into that of oxide. And both sulphate and oxide are capable of affording oxygen by a continuation of the process to the sulphuret, and thus sulphurous acid being disengaged, the metal will be reduced. The materials present with the lead, as lime and quartz, form a slag, to which, at a particular stage of the process, the temperature being lowered, more lime is added, so that the slag may become more solid, and allow the lead to be run out of the furnace.

The process of refining lead, and separating the silver which it contains, affords a beautiful illustration of the application of science to the arts. Formerly lead was separated from silver by the process of cupellation, which consists in burning off the lead in a current of hot air, in the form of litharge. Now, as this litharge often requires to be again reduced to the form of lead, a great saving was effected by diminishing the quantity of lead which required to be cupellated. This was done from the discovery of a property of the alloy of lead and silver, little to be expected from *a priori* considerations. When such an alloy, on being melted, is allowed to cool, the lead crystallises out first; consequently, when lead containing silver, say to the extent of 20 ounces in the ton, is melted in an iron pot, and the crystals which form

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in cooling are removed by a perforated ladle, the lead removed will contain less silver than what is left behind, so that at last what remains will contain perhaps 40 ounces to the ton. To both the portions the same processes of condensation are applied, so that at last the whole lead comes to be divided into two portions, the one containing perhaps 200 ounces to the ton, and the other almost free from silver, and much improved in many qualities by the process;—only the former is cupellated.

Lead has very little ductility; it melts at 612°, and contracts on cooling very considerably. It crystallises in octahedrons. When exposed to air and moisture, lead rapidly tarnishes, and the crust of oxide which forms, protects the rest of the metal from further action, unless it is exposed to the continuous action of water, which dissolves the oxide. Although only a 1-12,000th part of oxide is thus taken up, it is sufficient to render *soft* waters kept in lead cisterns, or passed through lead pipes, highly deleterious; but the presence of salts to any extent in water, and especially of carbonates and sulphates, causes salts of lead to be formed, on which the water has no further action. Hence perfectly pure water would be the most dangerous, if allowed to remain in lead cisterns.

Lead forms 3 distinct oxides—the Suboxide, $Pb_2O$; the Protoxide, $PbO$; and the Peroxide, $PbO_2$. It is not easily oxidated by acids.

### Suboxide of Lead, $Pb_2O$;

Is a dark-grey powder, formed by heating the oxalate in close vessels to redness. The oxalate is obtained by the action of oxalic acid on a soluble salt of lead.

### Protoxide of Lead, $PbO$; Eq. 111·56;

Is obtained by exposing lead at a high temperature to the action of a current of air; the yellow protoxide is then formed, and can be removed by skimming from the surface of the melted metal. The formation of this may be readily shown, by decomposing some sugar of lead, by heat, in a crucible. This substance is called *massicot;* melted by a stronger heat, it forms a brick-red mass, composed of crystalline scales, which is called *litharge.* Perhaps the pure protoxide is best prepared by igniting the nitrate, and may be precipitated as a white hydrate from its soluble salts by means of potassa. All its salts are acted upon by sulphuretted hydrogen—even the sulphate. Zinc and iron remove the metallic lead from these salts in solution.

### Peroxide of Lead, $PbO_2$;

May be prepared in the same way as the peroxides of cobalt and nickel. It is of a dark-brown colour. It forms no salts.

*Minium,* or red lead, is a mixed oxide, prepared by exposing massicot to low redness in a peculiarly shaped furnace, and urging it with a current of air. Its composition is variable, but that generally given is $2PbO+PbO_2$. When minium is treated by strong acids, it

is resolved into the protoxide, which forms a salt with the acid, and peroxide, which remains behind.

## Chloride of Lead, PbCl; Eq. 139·16;

Is easiest obtained by digesting oxide of lead in muriatic acid, or by precipitating a pretty strong solution of a salt of lead by an alkaline chloride. This compound is soluble in 135 parts of cold water. It crystallises from its hot solution in needles. It is an exceedingly fusible body.

## Iodide of Lead, PbI; Eq. 229·92;

Is thrown down in the form of a beautiful yellow powder, when solution of iodide of potassium is added to a soluble salt of lead. It is a much more insoluble salt than the chloride.

## Sulphuret of Lead, PbS; Eq. 119·56;

Is thrown down as a black powder whenever sulphuretted hydrogen is passed through a solution of a salt of lead; but the precipitate thus obtained, when *heated* in acid solutions, is readily dissolved, with escape of sulphuretted hydrogen gas. It is in this form that lead exists in galena.

*Carbonate of Lead—Ceruse, or White Lead* — $PbO,CO_2$, Eq. 133·56—occurs native; may be formed by adding an alkaline carbonate to a solution of acetate of lead. When precipitated in this way from solutions, it has a crystalline structure, which renders it unfit for the purpose of a pigment, for which it is generally manufactured. It is generally prepared by what is termed the Dutch method. For this purpose it is first cast into pieces, of a form which will allow the air to pass through them, something like a gridiron, and these are placed over earthenware vessels containing weak acetic acid, which are imbedded in fermenting tan. The quantity of vinegar required is so small, as to show that the lead is not oxidated by it. The oxygen must come from the air, and the carbonic acid from the tan.*

*Sulphate of Lead*, $PbO,SO_3$.—This salt is formed when a soluble salt of lead is treated with sulphuric acid, or an alkaline sulphate.

*Nitrate of Lead*, $PbO,No_5$.—Prepared by dissolving litharge, with the aid of heat, in nitric acid. The solution concentrated yields white octahedral crystals. By boiling this nitrate with metallic lead, brilliant yellow crystals of *nitrite of lead* may be obtained.

*Acetate of Lead*, PbO, $C_4H_3O_3+3HO$, is prepared by dissolving litharge in acetic acid. It crystallises in four-sided prisms, which are remarkable for their sweetish, slightly-astringent taste. They are

* Many attempts have been made to substitute other processes for the old Dutch mode of preparing white lead, and many to substitute other compounds of lead for it as a pigment, but hitherto with dubious success. The sulphate, the oxychloride prepared by the action of supercarbonate of magnesia or chloride of lead, have been proposed, and lately the arsenite, for some specific purposes.

soluble in less than twice their weight of water at 60°. When oxide of lead is boiled in solution of the acetate, a bibasic acetate is formed, and other basic acetates may be formed.*

### TESTS FOR LEAD.

These are very numerous. The following may be enumerated :— 1st. The action of iron and zinc on the solutions of lead, whereby beautiful crystalline plates of metallic lead may be formed on pieces of these metals, suspended for some time in solutions of salts of lead. 2nd. The action of sulphuretted hydrogen on all salts of lead. 3rd. The formation of a yellow precipitate when solution of iodide of potassium is added to these salts. 4th. The formation of a similar precipitate with red chromate of potass.

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## 37. BISMUTH, Bi.

Eq. 70·95; sp. gr. 9·53. Bismuth generally occurs native, and may be separated from the ores in which it exists by simple fusion.† Bismuth is a white crystalline metal, which melts at about 500°. It is volatilised at a red heat, and burns with a bluish flame, and formation of fumes of oxide of bismuth. It is not acted on by air, but dissolves readily in acids, in muriatic acid with evolution of hydrogen, and in nitric with evolution of compounds of nitrogen and oxygen. It has 3 oxides—a suboxide and a peroxide of little importance, and the

### PROTOXIDE OF BISMUTH, BiO ; Eq. 78.95 ;

Which is formed when the metal is burnt in the air, or by igniting the nitrate. It is a yellow powder, and is the basis of the salts of bismuth.

The most important salt of bismuth is the nitrate $BiO,NO_5+3HO$ ; eq. 133·33 + 27 ; it is obtained by the action of nitric acid, sp. gr. 1·42, on bismuth. The metal is dissolved with great rapidity, and on the solution being allowed to cool, crystals are obtained. These are four-sided prisms isomorphous with the analogous nitrate of magnesia. They are highly deliquescent. When thrown into water they are decomposed, and a compound, formed of three equivalents of oxide of bismuth with one of nitrate of water—that is to say, two equivalents of acid and water are removed from three of the neutral nitrate, and by long-continued washing all the nitric acid can be removed. The suboxide formed in

* Lead forms several alloys, principally with tin. These are the solders most in use.—Fine solder is 2 of tin and 1 of lead; it melts at 360°. Coarse solder contains ¼th of tin, and melts at 500°.

† Pure bismuth is obtained by igniting the nitrate, and reducing the oxide thus obtained with charcoal. Its equivalent by many is trebled. This will depend a good deal on whether we choose to rank it in the class with zinc or antimony. Here it is made to rank with zinc, and the eq. 70·95 retained.

this way is that used in medicine, and called also the trisnitrate. Under the name of flake white it has been used as a cosmetic.

The chief uses of bismuth are in forming alloys. These are very fusible. Eight parts of bismuth, five of lead, and three of tin, form a substance known as Newton's fusible alloy, which melts at 203°, and is employed in taking moulds. Bismuth, owing to its property of expanding when cooling, is also used in the metal for types, which is thus caused to take the finest impressions when cast into the type moulds.

Bismuth may be recognised by the action of sulphuretted hydrogen on its salts giving rise to a black precipitate; by the action of water in decomposing most of them; by yellow prussiate of potass giving a white precipitate with them; and by its oxide fusing before the blow-pipe, being dark-brown when hot, yellow when cooled, and being reduced on charcoal, and giving a colourless bead when fused with borax.

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SECT. 5.—OTHER METALS, HAVING ISOMORPHOUS RELATIONS WITH THE MAGNESIAN FAMILY, but differing in many respects from the preceding class, so that they are put into a separate class.—These are, Tin, Titanium, Chromium, Vanadium, Tungsten, Molybdenum, Tellurium.

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### 38. TIN, SN (STANNUM).

Eq. 58·82; sp. gr. 7·28. Tin occurs in nature chiefly in the form of the deutoxide, which is generally associated with other metals, and especially with arsenic. It is found in two forms in Cornwall—either in veins traversing the primary rocks, where it is more apt to be associated with other metals, or in rounded grains which have been exposed to the action of water, and deposited in beds of clay or gravel. The latter is called stream tin, and is much the purer form. The metal is obtained chiefly by roasting the ore with charcoal or coal, and then fusing it at a certain temperature, and stirring it repeatedly; the greater part of the impurities are driven off by the former process, and, in the latter, their separation completed, by the greater fusibility of the tin. Tin melts at 442°; on cooling, it crystallises; like most metals, it assumes the octahedral form, but the usual crystals are prisms. Owing to this crystalline character, when a bar of tin is bent it crackles. Tin is hardly volatile. It is little liable to oxidate in the air, a circumstance to which many of its most valuable properties are owing. It is very malleable, but has little tenacity. When melted in air, it is covered with a film of oxide, and, at a white heat, it burns. Nitric acid pure does not act on tin, but, if a little diluted, a violent action takes place, compounds of

oxygen and azote, with some ammonia are disengaged, and metastannie acid, $Sn_5O_{10}$, formed.   Muriatie acid readily dissolves tin; sulphurie acid more slowly.

Tin forms several compounds with oxygen, of which the more definite are, the Protoxide, SnO; the Deutoxide or Binoxide, $SnO_2$; and the compound already named Metastannie Acid.

### Protoxide of Tin, SnO; Eq. 66·82;

Is obtained by the action of solution of an alkaline earbonate on solution of chloride of tin.   There is no carbonate precipitated, but a white hydrate of the protoxide, which may be washed and dried at a temperature below 176°.   Dried and heated in an atmosphere of earbonic acid, it yields the anhydrous oxide in the form of a black powder.   This oxide may be obtained in different forms by various processes, furnishing thus a good illustration of allotropy.   For instance, if the solution of chloride of tin be decomposed by potassa instead of the carbonate, and the precipitate redissolved by excess of the alkali, and the whole evaporated in vacuo (see potassa, fig. 26), then black erystals of the oxide are formed, aud, by a somewbat similar process with ammonia, a red oxide may be obtained.   When oxide of tin is heated in the air it burns with great facility, and is eonverted into the deutoxide.

### Deutoxide of Tin, $SnO_2$; Eq. 74·82;

Termed also stannie acid.   Stannic acid is prepared as a hydrate by precipitating a solution of bichloride of tin with a solution of an alkaline carbonate.   The precipitate should be well washed.   When this preeipitate is dried in *vacuo*, it forms gummy-like masses, in which one eq. of water is combined with one of the peroxide.   The peroxide in this state is quite soluble in muriatie acid; but if it is digested for some time in boiling water, it is then fouud only to be very partially soluble in muriatie acid.   It may also be obtained by throwing the bichloride of tin into water.   This body can be made to form compounds called *stannates* with alkalies, and it even forms a *stannate* with the protoxide itself, which is also as a base termed a sesquioxide.

### Metastannic Acid, $Sn_5O_{10}$,10HO;

Is obtained when tin is acted ou by nitrie acid.   It is a erystalline powder, which is found to contain 10 eq. of water.   Dissolved in potass it forms the metastannate of potass.

### Chloride of Tin (Protochloride), SnCl+3HO; Eq. 94·32+27;

May be prepared by distilling a mixture of equal parts of ealomel and tin at a red heat.   It may also be obtained in the form of hydrate by dissolving tin in muriatie acid, diluted with an equal weight of water.   A portion of the metal is left undissolved, aud, on evaporating the solution, aeicular erystals are obtained.   This salt dissolves readily

in water, but is decomposed by a large quantity of this fluid in some-
thing of the same way that the salts of bismuth are decomposed, a
portion of chlorine being removed by the water in the form of muriatic
acid, and the bismuth of that portion oxidised, so that an oxichloride
is formed, $2SnCl + HO = SnCl,SnO + ClH$. This salt absorbs
oxygen rapidly from the air, and when added to solutions of many
metals, reduces them to the metallic state. It also absorbs colouring
matters from their solutions, and hence is used as a mordant.

### BICHLORIDE OF TIN, $SnCl_2$; Eq. 129·82.

The anhydrous bichloride known as the fuming liquor of Libavius,
may be obtained by distilling four parts of corrosive sublimate, mixed
with one of tin-filings.* A colourless liquid is distilled over. It fumes
in the air. When mixed with water it is solidified, forming a crystal-
line hydrate, in which two eq. of the bichloride are combined with five
eq. of water.

### SULPHURETS OF TIN, $SnS$, $SnS_2$.

The protosulphuret may be obtained by the direct union of tin and
sulphur, or by passing sulphuretted hydrogen through a solution of a
protosalt of tin; the black sulphuret is precipitated. The bisulphuret
is called mosaic gold, and is used for the coarser kinds of gilding. For
this purpose it must be prepared in the *dry way*. This is done by
heating in a covered crucible a mixture of twelve parts of tin, seven of
sulphur, and six of muriate of ammonia. When thus prepared it is in
bright yellow scales. When thrown down from solutions of the persalts
of tin by sulphuretted hydrogen, this substance is of a dirty yellow colour.

The salts of the oxide of tin are of little moment. The salts of tin
may be recognised thus,—those of the protoxide, by their giving metallic
tin when heated, by the effect of sulphuretted hydrogen, and prussiate
of potass giving a white precipitate. Those of the peroxide give the
precipitate described with sulphuretted hydrogen, and a yellow preci-
pitate with prussiate of potass.

Tin forms alloys of great value. With antimony, copper, and
bismuth it forms pewter. In the state of foil, it is used for preserving
many substances from the air; and for this purpose also it is employed
to cover iron, forming the substance generally known as tin-plate. It
is also used, amalgamated with mercury, to silver looking-glasses, and
forms, besides, a variety of useful alloys.

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### 39. TITANIUM, Ti.

Eq. 24·29; sp. gr. 5·3; Is found in nature in several minerals,
rutile, anatase, &c., almost pure, except that it is not native, but

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* It may also be obtained by the direct union of chlorine and tin, as
by passing a stream of chlorine over tin-foil or granular tin.

combined with oxygen, or in ores combined with iron. It is obtained by reducing titanic acid with charcoal, by the highest heat of a wind furnace, or such a blast furnace as in fig. 31. Titanium is a dark-green powder, infusible, which, when heated in air, burns, and forms titanic acid. Acids do not act upon titanium, except a mixture of hydro-fluoric and nitric acids. It forms three oxides—a Protoxide, TiO; a Sesquioxide, $Ti_2O_3$; and a Peroxide, termed titanic acid, $TiO_2$.

### PROTOXIDE OF TITANIUM, TiO;

Is produced when titanic acid is heated intensely in a crucible lined with charcoal; the acid near the charcoal is reduced to the metallic state; but that in the centre of the masses is changed into the oxide. It is a black substance. It is also formed by heating titanic acid with potassium. It is scarcely soluble in acids and alkalies.

### SESQUIOXIDE OF TITANIUM, $Ti_2O_3$;

Is obtained by passing a current of hydrogen over titanic acid strongly heated. It may also be obtained by the action of an alkali on the sesquichloride. It rapidly absorbs oxygen, and becomes titanic acid.

### TITANIC ACID, $TiO_2$; Eq. 40·29;

Is the form in which titanium exists native. It is obtained by heating rutile with chloride of barium. By this, after the mass has been freed by washing from excess of chloride of barium, a titanate of baryta and peroxide of iron are obtained. By the action of sulphuric acid and water, titanic acid and sulphate of iron are obtained in solution, and sulphate of baryta left behind; sulphuretted hydrogen is passed through the solution to get rid of any tin which may exist; and then ammonia is added to neutralise the solution; titanic acid is thrown down. It is digested with solution of sulphurous acid, to free it from any sulphuret of iron, and then the titanic acid washed remains pure. Titanic acid is a white powder, infusible and insoluble in water. When previously heated with an alkaline carbonate, it becomes soluble in muriatic acid. The solution gives a yellow colour with infusion of galls, characteristic of this acid. When this solution is neutralised by ammonia, a gelatinous precipitate is thrown down, which is this soluble titanic acid. On this being collected, dried, and heated, it becomes incandescent, and loses its property of solubility.

### CHLORIDES OF TITANIUM.

A Sesquichloride and a Bichloride are known.

### SESQUICHLORIDE OF TITANIUM, $Ti_2Cl_3$;

Is obtained by passing through a tube heated to redness, vapour of hydrogen, which has been made to absorb bichloride of titanium at a red heat; crystals of the sesquichloride form in the cool part of the tube. The effect of the hydrogen is to deprive the bichloride of a

portion of its chlorine. The sesquichloride is found thus prepared in violet scales, and presents very remarkable desiccating properties.

### BICHLORIDE OF TITANIUM, $TiCl_2$;

Is produced by passing chlorine over metallic titanium at a red heat. It is a colourless liquid, and boils at the same temperature as water.

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## 40. CHROMIUM, Cr.

Eq. 28·15.; sp. gr. 5·9. This metal exists native in several minerals, amongst which may be particularly mentioned the chromates of lead and chrome-iron. The latter substance is an ore of the composition $FeO + Cr_2O_3$. When this ore is calcined with carbonate of potass, with or without some nitrate, in a reverberatory furnace, the oxide of chromium, by absorption of oxygen, is converted into chromic acid, which combines with the potass forming chromate of potass. At the same time the iron is peroxidised. By lixiviating the mass, a mixture of carbonate and chromate of potass is obtained. The addition of sulphuric acid gives rise to a bichromate and a sulphate. As this former salt is much the more soluble, the two can be separated by crystallisation. Metallic chromium is obtained by reducing the oxide in a crucible lined with charcoal, in a blast furnace. It is of a greyish-white colour, very infusible. It is not oxidated in the atmosphere at ordinary temperature. Acids act upon it with difficulty, but, heated with alkalies, it forms chromic acid. It forms four compounds with oxygen—the Oxide, or Protoxide, $CrO$; the Sesquioxide, $Cr_2O_3$; Chromic Acid, $CrO_3$; and Perchromic Acid, $Cr_2O_7$. The existence of the first is doubtful, or at least it is soon resolved into a mixture of oxide and sesquioxide by absorption of oxygen.

### SESQUIOXIDE OF CHROMIUM, $Cr_2O_3$; Eq. 80·30;

Is obtained by igniting the chromate of mercury; in the first place, solution of chromate of potass and nitrate of mercury are mixed, and the precipitate which forms is then ignited. It is thus obtained as a green powder; but it may be procured in the form of very dark-green crystals, by passing the vapour of chlorochromic acid through a tube heated to an intense heat. The chlorochromic acid (see its formula) is decomposed, and oxide of chromium forms in the cooler portion of the apparatus. In these forms it is not soluble in acids. It may be obtained as a hydrate soluble in acids, by adding hydrochloric acid and alcohol alternately to a boiling solution of bichromate of potass.

This substance is very useful in colouring stone-ware pink.

### CHROMIC ACID, $CrO_3$; Eq. 52·15;

May be obtained by passing fluosilicic acid, prepared by heating in a glass retort, fluor spar, sulphuric acid and glass, into a hot solution

of bichromate of potass.* The potass is removed by the formation of a fluosilicate of potassa, or fluoride of silicon and potassium, which is insoluble. The solution, evaporated to dryness, gives a residuum, which is to be redissolved for use. It forms a yellow solution. This acid is a very powerful oxygenating agent, bleaches like chlorine, and, in doing so, is reduced to the state of sesquioxide. It combines with several bases, and possesses considerable chemical power. Its salts are distinguished by their splendid colours. The solution exposed to the light loses a portion of its oxygen, and the sesquioxide formed combines with another eq. of chromic acid, and forms a chromate of that base.

SALTS OF CHROMIC ACID. The *Chromate of potass* is prepared by the addition of carbonate of potass to a solution of the bichromate, which latter is obtained, as described, from chrome ore. It crystallises in double pyramids of six faces, or in oblique four-sided prisms, isomorphous with the sulphate. These are of a beautiful yellow colour. The *bichromate* crystallises in fine red tables. The *chromate of lead*, known as chrome yellow, a fine yellow salt, is obtained by the reaction of salts of lead and chromates of potass. The *subchromate of lead* is obtained when an equivalent of chromate of potass, one of free potassa, and one of nitrate of lead, meet together; the equivalent of alkali retains half an equivalent of the chromic acid. Chromate and nitrate of potass can be removed by washing, and the red subchromate remains. All these salts are much used in dyeing, and as pigments.

## PERCHROMIC ACID, $Cr_2O_7$ ;

Is a very unstable acid, and soon passes into the sesquioxide by loss of oxygen. It may be formed by the action of oxygenated water on the former compound.

## CHLORIDE OF CHROMIUM, $Cr_2Cl$.

Obtained by heating sesquioxide in a current of chlorine. It rapidly absorbs oxygen from the air, and forms an oxychloride.

## SESQUICHLORIDE OF CHROMIUM, $Cr_2Cl_3$.

A solution of this substance may be procured by dissolving the hydrate of the sesquioxide in muriatic acid. It is of a fine green colour.

## CHLOROCHROMIC ACID, $CrCl_3$, $2Cr_2O_3$ ;

May be obtained by distilling in an ordinary retort 3 parts of bichromate of potass, and $3\frac{1}{2}$ parts of the muriate of soda, triturated

* Equal parts of pounded fluor spar, and glass, with six parts of strong sulphuric acid, are to be used. For the theory of the process see Fluorine. The fluorilic acid is to be passed into the solution as long as any potass remains, which can be ascertained by testing.

together along with 5 by measure of sulphuric acid. A red liquid will be found in the receiver. This also is a powerful oxidating agent. Water resolves it into chromic and muriatic acids.

The compounds of chromium are easily recognised by their striking reactions.

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## 41. VANADIUM, V.

Eq. 68·55. A very rare metal, which has been found associated with iron and lead. In its general properties, it bears some relation to chromium. It forms three compounds—the protoxide, $VO$; the binoxide, $VO_2$; and the teroxide, $VO_3$, which has acid properties, and is called vanadic acid. The salts are formed by the second compound. The vanadic acid, from which the other oxides are formed, may be prepared by dissolving the natural vanadiate of lead in nitric acid, precipitating lead and arsenic by sulphuretted hydrogen; there is then a blue solution of binoxide of vanadium, which, on being evaporated to dryness, forms vanadic acid. Vanadic and chromic acids both form red solutions; but the former becomes blue, and the latter green, when they are deoxidised.

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## 42. TUNGSTEN, W.

Eq. 94·64; sp. gr. 17·6. Exists chiefly in the mineral called wolfram, where it is in the form of tungstic acid. The metal is prepared from the tungstic acid by the reducing action of hydrogen at a high temperature, or in the way in which manganese and similar metals are reduced by charcoal. It is a dark-grey, almost infusible metal. In specific gravity it is next to gold and platinum. As it is obtained by reduction with hydrogen, it is in the spongy form, and takes fire in air, being converted into tungstic acid. It forms two compounds with oxygen—the tungstic oxide, $WO_2$; and the tungstic acid, $WO_3$. The former is prepared when the latter is exposed to a current of hydrogen at a low red heat. The latter is obtained from wolfram by simply acting on the ore with aqua regia, which dissolves out the iron and manganese. The residue, after being washed, is dissolved in ammonia, whereby a tungstate of ammonia is formed; and the solution evaporated and ignited leaves tungstic acid. Tungstic acid is a yellow solid, which by heat loses a portion of its oxygen, and is converted into a compound with the oxide. This is of a blue colour. Tungstates are readily formed with alkalies, as may be seen, from the action of ammonia; but the acid is perfectly insoluble in water and acids. Tungsten forms compounds with chlorine sulphur, &c.

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## 43. MOLYBDENUM, Mo.

Eq. 47·88; sp. gr. 8·52. This is a very rare metal, in many respects closely resembling tungsten, but differing, as will be seen, greatly in weight. It occurs in nature in the form of a sulphuret, closely resembling plumbago, or in the form of molybdate of lead. It may be prepared from molybdic acid by processes precisely analogous to those for tungsten. It is a white metal, which is not acted on by dilute acids, but soluble in aqua regia, nitric acid, or strong sulphuric acid. It forms three oxides — the protoxide, $MoO$; the binoxide, $MoO_2$; and the teroxide, termed molybdic acid, $MoO_3$. The first is best prepared by dissolving one of the salts of the acid in hydrochloric acid, and introducing a piece of zinc. The solution undergoes several changes of colour; and chloride of zinc and protochloride of molybdenum are formed. Ammonia is then added carefully to the fluid, so as to throw down the oxide of molybdenum, and leave the zinc, some oxide of zinc carried down is removed by repeated washing with ammonia, when the black hydrate of the oxide of molybdenum remains. It is scarcely soluble in acids. The binoxide may be obtained mixed with a little protoxide, by igniting the molybdate of ammonia in a covered crucible. Prepared in this mode, it is insoluble in acids. It may be procured hydrated by dissolving molybdic acid and copper in muriatic acid, and adding excess of ammonia, which precipitates the binoxide, and leaves the copper in solution. This hydrate forms salts with acids, which are red when hydrated, and crystallised and black when anhydrous. The molybdic acid is obtained by roasting the native sulphuret, dissolving the residue in ammonia, and then crystallising and igniting the crystals of molybdate of ammonia. It is left as a porous substance, which melts at a red heat, and then assumes a crystalline structure on cooling, and is of a yellow colour. Its salts are colourless, when the base is so. They are readily formed. When molybdenum is heated in an atmosphere of chlorine, it forms a dark-red gas, which is deposited in crystals like iodine, analogous to the chlorochromic acid.

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## 44. TELLURIUM, Te.

Eq. 66·14; sp. gr. 6·25. This is another rare metal, found in conjunction with gold, silver, lead, and bismuth, which presents several analogies with sulphur. Tellurium may be obtained from the tellurite of bismuth, by heating it with carbon and carbonate of potass. In this process, metallic bismuth and a tellurite of potassium is formed. The latter is soluble, and from the solution tellurium is gradually deposited. Tellurium is a brilliant silvery metal. It can be crystallised in rhombohedral crystals, isomorphous with those of arsenic and antimony. It melts at

about 800°, and volatilises at a higher temperature. It burns when heated in the air, forming tellurous acid, $TeO_2$. The same acid may also be obtained by other processes, as by decomposing bichloride of tellurium by cold water. It is a white earth-like substance, generally crystalline, readily soluble in acids and in alkalies, with which it forms tellurites. The telluric acid, $TeO_3$ may be prepared first by fusing tellurous acid with nitre, and thus forming a tellurate of potash, which may be decomposed by hydrate of baryta, and the insoluble tellurate of baryta by sulphuric acid. It may be crystallised from its solutions along with 3 eqs. of water. The bichloride of tellurium may be prepared by heating tellurium in chlorine. Telluretted hydrogen, a gas similar to sulphuretted hydrogen, is obtained by fusing tellurium with tin or zinc, and treating the result with muriatic acid. Sulphuretted hydrogen gives a brown precipitate with the salts of tellurous acid, and a black with those of telluric acid; alkalies and alkaline carbonates a white precipitate with the tellurites, soluble in excess of the reagent.

Sect. 6.—METALS ISOMORPHOUS WITH PHOSPHORUS.—These include Arsenic, Antimony, and Bismuth.*

## 45. ARSENIC, As.

Eq. 75; sp. gr. 5·75. Arsenic occurs native—mostly along with other metals; generally it is found as a sulphuret in combination with other metals, as iron, cobalt, and nickel. It is generally obtained by roasting the sulphuret with the addition of iron, which retains all the sulphur, while the arsenic is oxidated and sublimed in the form of arsenious acid. To obtain metallic arsenic, the arsenious acid is mixed with twice its weight of black flux,† and heated in a crucible, within which another crucible is inserted and inverted. The crucibles are luted together, and a little hole is made in the upper, or, better still, a bent tube connected with the upper part. The upper crucible should be kept cool. The arsenic sublimes into the upper crucible. A little can readily be made in a glass tube or retort. Arsenic crystallises in rhombohedrons. It is a very brittle metal. It sublimes at 360° without

* Bismuth has already been treated of, on account of its resemblance to lead.

† Black flux is prepared by igniting cream of tartar, or bitartrate of potash. It is the same substance as is used in preparing potassium. Its carbonate of potass takes the sulphur, and its carbon prevents, or helps to prevent, the oxidation of the arsenic.

previously melting. It has a smell like garlic, and forms two compounds with oxygen—$AsO_3$, or arsenious acid; and $AsO_5$, arsenic acid.

## Arsenious Acid, $AsO_3$; Eq. 99 (Arsenic—White Arsenic);

Occurs in two forms, as obtained by sublimation, and as sold in commerce unground. Some is opaque and quite white; another kind of a more vitreous character, yellowish and translucent. These varieties differ in density, the latter being 3·738, the former 3·369. The opaque kind is also more soluble—100 parts of water at 212° dissolving 11·47 of it, while they only dissolve 9·68 of the vitreous; and when the solutions cool to 60°, 2·9 of the former remain in solution, and only 1·78 of the latter. Arsenic, therefore, is another instance of allotropy. Arsenious acid volatilises below a red heat. When arsenious acid is slowly sublimed in a glass tube, it crystallises in regular octahedrons. It occurs sometimes in prisms. Arsenious acid boiled with alkaline solutions combines with them. It also forms salts with metals, some of which are very definite.

## Arsenic Acid, $AsO_5$; Eq. 115 ;

Is obtained by digesting arsenious acid with nitric acid, as long as red fumes are disengaged. The mass is then dried and heated to expel excess of nitric acid. It must not, however, be heated above 600°, for above that temperature it is resolved into arsenious acid and oxygen. Arsenic acid is a white solid, which deliquesces when exposed to the air. Arsenic acid is distinctly sour, while arsenious acid is not. When arsenic acid is heated with excess of carbonate of soda, it forms a tribasic arseniate isomorphous with the corresponding subphosphate, having a formula $3NaO,AsO_5 + 24HO$. By adding carbonate of soda to a hot solution of arsenic acid as long as carbonic acid is expelled, and then evaporating, a salt is obtained corresponding to the common phosphate of soda—*i. e.*, containing two of soda and one of basic water. Like common phosphate of soda, it sometimes has 14, sometimes 24 eqs. of water of crystallisation, forming $2NaO,HO,AsO_5 + 14HO$. This salt is more soluble than the phosphate. When to this salt an eq. of arsenic acid is added, a binarseniate is formed corresponding to the biphosphate. But those changes which take place on phosphoric acid itself cannot be imitated by arsenic acid; because, although these salts, like the phosphates, lose their water at a red heat, they recover it again when redissolved. Arsenic acid, therefore, only forms one class of salts. The alkaline arseniates are soluble; the metallic ones insoluble.

### CHLORIDES OF ARSENIC.

A subchloride is supposed to exist. The ordinary chloride corresponds to arsenious acid. It may be formed directly by introducing metallic arsenic into chlorine gas. The arsenic takes fire. It may also be obtained by distilling the metal with six parts of corrosive sublimate. A similar bromide and iodide may be formed.

## SULPHURETS OF ARSENIC.

Of these there are several; but the chief are, the tersulphuret, called also orpiment and sulpharsenious acid, having a formula of $AsS_3$, which is prepared by decomposing a solution of arsenic in muriatic acid by sulphuretted hydrogen, or an alkaline sulphuret. When heated it melts, and then sublimes. It combines with alkaline sulphurets as an acid, forming double salts. Heated with black flux it yields metallic arsenic. The sulpharsenic acid, or realgar, is formed when sulphuretted hydrogen is passed through arsenic acid. Its formula is $AsS_5$. It is very like orpiment, readily melts, and acquires a red colour, and sublimes at a low temperature; it is a more powerful sulphur acid than the former compound.

## ARSENIETTED HYDROGEN, $AsH_3$;

Is obtained from the mutual action of zinc and sulphuric acid. The arsenic combines with the hydrogen disengaged, and arsenietted hydrogen is obtained. Arsenietted hydrogen has a garlic smell, somewhat similar to that of metallic arsenic. Its sp. gr. is 2·69; it is soluble in water; when inflamed in air, the products of its combustion are arsenious acid and water. It is decomposed by chlorine with combustion.

Arsenic forms numerous alloys with metals. Its principal use this way is to harden tin.

## TESTS FOR ARSENIC.

The metal may be recognised by subliming it, and by its solution in hydrochloric acid, giving the characteristic results obtained with arsenious acid.

Arsenious acid is detected in two ways—first, by what are termed fluid tests, and also by what are called reduction tests. The principal fluid tests are—1st, The ammonio nitrate of silver, which gives a yellow precipitate with solutions of arsenious acid. The presence of ammonia enables the arsenious acid to take the place of the nitric, by the affinity of the ammonia for the latter—arsenite of silver and nitrate of ammonia being formed. 2nd, The ammonio sulphate of copper gives a green precipitate, called Scheele's green. 3rd, Sulphuretted hydrogen throws down a yellow precipitate. Although objections may be taken to these tests separately, yet if they all give these results, no objection applies to the inference from the three of the presence of arsenic, since there is no substance whatever which would give all these three results, but arsenic. If arsenious acid is in the solid form, it can be heated, when it will be sublimed in octahedral crystals, which may require to be examined with the miscroscope if the quantity be small; or it may be heated in a tube, when a sublimate of metallic arsenic will be obtained; or it can be boiled in water, and the fluid tests applied to the solution. The reduction tests are—1st, The obtaining

of the metal from the sulphuret in a tube, as in fig. 32, by heating it with black flux. 2nd, Marsh's test, which consists in acting upon the suspected solution with zinc and sulphuric acid, in an apparatus like that in fig. 33. Here the solution should *nearly* touch the cork to which the stopcock is attached; on turning the stopcock, if arsenic be present, arsenietted hydrogen will be evolved; on inflaming this, and holding a porcelain plate close to the hole of the jet attached to the stopcock, it will receive a fine hair-brown stain of metallic arsenic. If, however, it be held at a distance, an opaque white spot will be produced. A glass plate is more suitable for this experiment. What takes place is this—the hydrogen of the arsenietted hydrogen is the more combustible of its two elements, and it burns first, so that when the porcelain is placed close to the jet, the arsenic not having time or space to burn, is deposited in the metallic form; but further off it has burnt too, and in that position it is deposited as white arsenious acid. 3rd, What is termed Reinsch's test, when solutions containing arsenic are acidulated with muriatic acid and boiled with copper, a black metallic coat of arsenic is thrown down on the copper. On heating this copper in a moderately wide tube (see fig. 34), it loses its black colour, and a ring of white octahedral crystals is obtained.

To these tests various objections have been made. Other metals as well as arsenic are precipitated by boiling their solutions with copper and muriatic acid; but then they do not sublime from it in the form that arsenic does. Cadmium gives a yellow precipitate with sulphuretted hydrogen; but the sulphuret is insoluble in ammonia, in which the sulphuret of arsenic may be dissolved. Antimony forms an antimoniuretted hydrogen gas, analogous to the arseniuretted, and which burns too; but the stain of antimony is of a sooty black, totally unlike the fine brilliant hair-brown stain of arsenic. The sulphuric acid and zinc employed may contain arsenic; this is obviated by testing them in the Marsh's apparatus *before* the suspected fluid is introduced. The test most open to fallacy is that of the sulphate of copper; for several substances give precipitates more or less green with ammonio sulphate of copper, and organic matter does so.

The great difficulty in testing for arsenic is the presence of organic matter. If a solution containing organic matter be put into a Marsh's apparatus, the frothing is so great as to impede the action of the apparatus; if organic matter be present when Reinsch's test is tried, some of it is precipitated upon the copper, and if the quantity of arsenic be small, it will impede the distinct appearance in the sublimate of octahedral crystals, and in the test by sulphuretted hydrogen, it will impede the reduction of the arsenic as a bright metallic crust.

The getting rid of organic matter in the contents of the stomach, or tissues of the body, is the great difficulty in searching for evidence of the presence of arsenic. For this several methods have been invented, especially since the discovery of the great physiological fact, that arsenic, like many other poisons, is absorbed into all the tissues of the body, and may be recovered from them. One very good way, when the contents of the stomach are in question, and they are not

very much overloaded with organic matter, is to boil them with water and a little nitric acid, then to strain through calico, precipitate the animal matter by excess of nitrate of silver, and the excess of nitrate of silver by common salt; then filter, and pass sulphuretted hydrogen through the solution, heat to collect the precipitate, and reduce. If the quantity of animal matter be not large, Marsh's test may be used, a large vessel being employed, as represented in fig. 35 or similar to the apparatus for making hydrogen, and the arsenietted hydrogen passed into a solution of nitrate of silver, when it gives a black precipitate of arseniuret of silver, which, on being heated in a tube, gives a ring of crystals of arsenious acid. But in general it is necessary to get rid of animal or other organic matter by burning it off: this is generally done by forming decoctions of the matter examined with acid solutions, concentrating them, and burning the animal matter off with the acid; then boiling the ash with a dilute acid, generally the muriatic, and applying tests to the solution. These processes require great nicety of manipulation. The details connected with them will be found in works of medical jurisprudence.



Fig. 33.

Fig. 34.

Fig. 35.

Fig. 32.
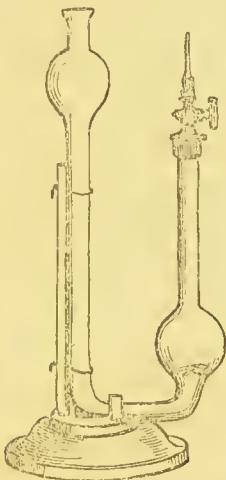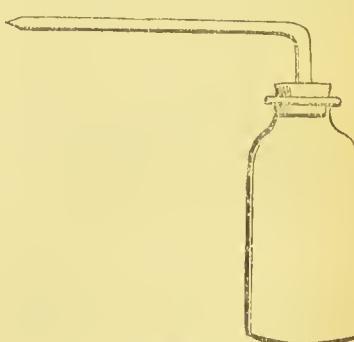
The alkaline arsenites, which are soluble, give similar results to arsenic itself. Arsenite of copper, on being heated in a tube, gives a crystalline ring of arsenious acid. Arsenic acid, &c., gives a red colour with solution of nitrate of silver. The best antidote to arsenious acid is the hydrated peroxide of iron, or magnesia.

## 46. ANTIMONY, Sb (STIBIUM).

Eq. 129·24, sp. gr. 4·7. This metal exists in nature mostly as a sulphuret. It is obtained from this by mixing four parts of it with one

and a half of nitre and three of crude tartar, and casting the mixture, in small quantities, into a red-hot crucible; or it is obtained by subliming the sulphuret from iron which takes the sulphur, or by igniting tartrate of antimony and potass iu a crucible, and then washing the residue. After what has been said of the reduction of arsenic from the sulphuret, the first and last of these processes will be readily understood. Antimony is a bright metal, isomorphous with arsenic, and which is not oxidated in the air at ordinary temperature. It melts at 797°; and is volatilised at a white heat, and burns at a red heat. Its best solvent is aqua regia. It forms three compounds with oxygen—the Teroxide, $SbO_3$, corresponding with arsenious acid; the Antimonic Acid, $SbO_5$, analogous to arsenic acid; and $SbO_4$, called Antimonious Acid.

### Oxide of Antimony, $SbO_3$; Eq. 153·28;

Is best prepared by dissolving the sulphuret in four times its weight of muriatic acid; sulphuretted hydrogen is evolved and chloride of antimouy formed and dissolved. The solution is treated with solution of carbonate of potass at the boiling point; carbonic acid is disengaged, chloride of potassium being formed, and oxide of antimony precipitated. It may also be obtained by the oxidation of metallic antimouy, and its sublimation iu au apparatus open to the air; and it is formed on the combustiou of antimouy. Oxide of antimony is white, but becomes yellowish when heated. It melts at a red heat, and sublimes at a higher temperature.

### Antimonious Acid, $SbO_4$,

Is produced by acting upon metallic antimony with nitric acid. When fused with potass, and the result is decomposed by an acid, it is procured as a hydrate, possessing an acid reactiou; by some it is considered a compound of the teroxide aud antimouic acid.

### Antimonic Acid, $SbO_5$,

Is prepared by oxidating the teroxide by means of uitric acid. It is obtained as a hydrate with five eqs. of water, when the autimoniate of potass is decomposed by dilute nitric acid. It is white, slightly soluble in water, and feebly reddens litmus. When heated, it loses water, and becomes yellow. It forms a class of salts called antimoniates. The antimoniate of potass is prepared by fusing one part of antimony in powder with four of nitre. The residue reduced to powder is well washed, the excess of potass is removed, and antimoniate of potassa remains. This is anhydrous, but, boiled iu water, it dissolves, aud the solution evaporated gives a salt containiug five eqs. of water. Here this acid combines with oue eq. of potassa; but it may be so prepared as to require two eqs. of base—it is then called Metantimonic Acid.

### CHLORIDES OF ANTIMONY.

There are two, analogous to the teroxide and antimonic acid.

Chloride of Antimony, $SbCl_3$; Eq. 335·7, is prepared in mauy ways; but a ready mode is to dissolve the sulphuret in strong muriatic acid,

as in preparing the oxides, and evaporating. It is the result when metallic antimony in fine powder takes fire in chlorine. It may also be obtained by treating one part of antimony with two of corrosive sublimate. It is a soft, deliquescent solid, and is called butter of antimony. It volatilises at a high temperature. It is decomposed by water, forming a white oxichloride, known by the alchemistical name of *Powder of Algaroth.*

PENTACHLORIDE OF ANTIMONY, $SbCl_5$. Prepared by heating powdered antimony in a current of chlorine; a receiver attached collects the liquid, which must be redistilled. It is a volatile fuming liquid, which is decomposed by water, hydrochloric and antimonic acids being formed.

The bromides and iodides of antimony may be formed: they are solid.

### SULPHURETS OF ANTIMONY.

There are two of these, corresponding with oxide of antimony, and antimonic acid.

### TERSULPHURET OF ANTIMONY, $SbS_3$; Eq. 177·24;

Is the common ore of antimony. As found in nature, it is often very impure. From some of its impurities it may be freed by levigation. Prepared from the native sulphuret, in this way it is black, and of a metallic appearance; precipitated by sulphuretted hydrogen from the tartrate of antimony and potass, it is red; but when this, which is a hydrate, is deprived of its water, it first becomes dull orange, and ultimately black. The levigated sulphuret is called, in the pharmacopœia, the prepared sulphuret. When this is dissolved by boiling in solution of carbonate of potass, and the solution filtered hot and left to cool, the sulphuret is deposited mixed with the oxide as an oxisulphuret, known as *Kermes'* mineral, of a reddish-brown colour. On adding sulphuric acid to the liquid after this deposit has taken place, there is a further precipitate of a mixture of the two sulphurets, called *golden sulphuret of antimony.* Glass of antimony is formed by heating the tersulphuret in air; it is composed partly of teroxide and partly of tersulphuret; the mode in which it is produced, it is not difficult to discover.

PENTASULPHURET OF ANTIMONY, $SbS_5$, is obtained by passing sulphuretted hydrogen through a solution of the pentachloride; it resembles in appearance the tersulphuret, but is of a much brighter colour. It is a powerful sulphur acid.

### ANTIMONIURETTED HYDROGEN, $SbH_3$,

Is produced in the same way as arseniuretted hydrogen, from which it is distinguished by the following circumstances:—1st, it burns with a much paler flame; 2nd, the stain it leaves is of the character already described, and, dissolved in acids, does not give the reactions of arsenic. Passed into a solution of nitrate of silver, it gives a black precipitate.

The most important salt of antimony is the body generally known as emetic tartar—the double tartrate of antimony and potass.

TARTRATE OF ANTIMONY AND POTASS, $KO,SbO_3 + (C_8H_4O_{10})2HO$ ;
Eq. $332.24 + 18$ ;

Is prepared by boiling oxide of antimony in four parts of water, with bitartrate of potass, adding the cream of tartar to the oxide in the water, until it is all dissolved. The solution is to be filtered, and, on cooling, furnishes a crop of crystals (octohedrons, with rhombic bases), which are at first transparent, but, exposed to the air, lose their water of crystallisation, and become white. They are soluble in fourteen parts of cold water, and in $1.88$ of boiling water. This salt was formerly considered a compound of tartrate of potass and tartrate of antimony. It is now found more suitable to double the equivalent of tartaric acid, and represent it as a bibasic acid. In this way the salt becomes a compound of two equivalents of base (one of oxide of antimony, and one of potassa, with one of tartaric acid).

### TESTS FOR ANTIMONY.

This metal is easily detected by the reaction of sulphuretted hydrogen on its salts, and also by Marsh's test. If any of the salts be introduced into a Marsh's apparatus, they will give the sooty black metallic deposit already spoken of. The sulphuret may be dissolved in hydrochloric acid, and the action of water on the solution observed.

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SECT. 7.—METALS NOT INCLUDED IN THE PRECEDING DIVISIONS, and whose Oxides are not reducible by heat alone. These are, Uranium, Cerium, Lanthanum, Didymium, Titanium, Tantalium or Columbium, Pelopium, Niobium. Titanium has already, on account of its other properties, been placed between tin and chromium.

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## 47. URANIUM, U.

Eq. 60; sp. gr. $9.0$. Uranium is obtained almost entirely from a mineral called *pitchblende*. In this mineral it is combined with lead, iron, and other metals, as arsenic and cobalt, and with silica. The metal itself is obtained by heating the chloride with potassium, and washing out the chloride of potassium formed. It is a bright metallic substance, somewhat malleable, which burns when heated in the air, and is converted into the green oxide of uranium, which is a compound of the protoxide and sesquioxide. There are three oxides of uranium—the suboxide, $U_4O_3$; the oxide or protoxide, which, until lately, was taken for the metal $UO$ ; and the sesquioxide or peroxide, $U_2O_3$. The first compound does not appear well determined. The second or black oxide, formerly taken for the metal, is obtained by passing a current of hydrogen over the oxalate of the sesquioxide at a red heat. It takes fire when heated in the air, and is converted into a black powder, another compound of protoxide and sesquioxide. The protoxide is

thrown down in the form of hydrate, on adding ammonia to one of its salts. The sesquioxide, the most important of these oxides, may be obtained by heating the nitrate to a temperature of 482 degrees. Its hydrate may be obtained by a peculiar process from the nitrate. It is yellow, and forms yellow solutions of salts. The protochloride is prepared by heating the protoxide mixed with charcoal, in an atmosphere of chlorine. It forms green octohedral deliquescent crystals. The nitrate is the most important salt, and from it most of the other compounds are prepared. It is obtained from the blende by digesting it in nitric acid, and evaporating the solution to dryness, when insoluble sulphate and arseniate of lead are formed. The mass is treated with water, and then sulphuretted hydrogen is passed through the solution, which throws down most of the other metals ; the filtered liquid is again evaporated to dryness, and the residue treated with water. A little peroxide of iron is left, and another solution in water obtained, and evaporated until it crystallises. The sesquioxide obtained from this nitrate is used for colouring glass and porcelain yellow.

## 48. CERIUM, LANTHANUM, AND DIDYMIUM.

These very rare metals occur native in the mineral cerite which is found in Sweden. It is doubtful whether they should not be classed with the metallic bases of the earths. On account of their rarity, it is not deemed requisite to do more than refer to them here.

Tantalum, Ta, or Columbium, Niobium, Pelopium, and Ilmenium, are metals of the rarest kind, and may be here simply enumerated. They are obtained from minerals known as tantalites and yttrotantalites.

SECT. 8.—METALS WHOSE OXIDES ARE REDUCED TO THE METALLIC STATE BY HEAT (noble metals), Mercury, Silver, and Gold.

## 55. MERCURY, Hg (HYDRARGYRUM).

Eq. 100·7 ; sp. gr. 13·595. Mercury is sometimes found native but its chief ore is the sulphuret known commonly as native sulphuret. From this the metal is obtained by distillation with iron or lime. In general, quicksilver found in commerce is very pure. If, however, it appears tarnished, or stains paper when it is run over, or does not form the round lively globule which mercury generally does ; if, in short, there is reason to suppose it impure, and it is desired to purify it, it may be digested with a little nitric or sulphuric acid, and then, after being well washed and dried, distilled off half its weight of iron filings.

Mercury does not oxidate in the air at ordinary temperatures. It freezes at—40°, and then is found crystallised in the form so many of the metals and elements assume—that of the regular octohedron. It boils at 662°. When heated for some time in air, it is oxidated. (See red oxide.) It is readily acted on by nitric acid and sulphuric acid, with the aid of heat, but not by muriatic acid.

### OXIDES OF MERCURY.

Suboxide, $Hg_2O$; Eq. 209·4. *Black Oxide.* It may be obtained in several ways, of which the readiest, perhaps, is to triturate calomel, the subchloride, with excess of solution of caustic potass. After collecting the oxide on a filter and washing it, it should be dried in the dark, as light appears to resolve it into the red oxide and metallic mercury. It forms salts with acids as well as the protoxide. Lime water precipitates it from its salts as well as the alkalies. By the alkaline carbonates it is thrown down white; but these precipitates soon lose $CO_2$, and become black. The other reactions of these salts, and their relations to those of the persalts, will be considered under the head of Tests for Mercury.

Peroxide, $HgO$; *Red Oxide,* $HgO$; Eq. 108·7—May be formed by heating mercury in a flask open to the air for a long time, at a temperature nearly approaching its boiling point. It is found at last oxidated in crystalline scales. It is always, however, obtained by the oxidation of mercury in nitric acid, with the aid of a gentle heat, and by applying heat until the nitric acid is expelled, and the residue, after ceasing to give off fumes, becomes a dark powder. This powder, on cooling, assumes the appearance of a fine red crystalline powder. Its sp. gr. is 11·074. The same oxide is obtained from its salts precipitated with caustic potass in excess. Its colour then is much lighter. It may be remarked, that these variations of colour in bodies of the same chemical composition, are not confined to one or two of the compounds of mercury. This substance is generally known as *red precipitate.*

### CHLORIDES OF MERCURY.

Subchloride, $Hg_2Cl$; Eq. 236·9. Calomel, also protochloride muriate, may be obtained in a variety of modes. That most generally employed is to triturate four parts of corrosive sublimate with three of metallic mercury, until the globules cease to appear, and, subliming, taking care to wash the sublimate; or the sulphate of mercury (of the red oxide) may be triturated with mercury and chloride of sodium, in the proportion of an equivalent of each, and the mixture sublimed. In the former of these processes the action is represented by the formula $Hg_2Cl + Hg = Hg_2Cl$; and in the latter it is $HgO,SO_3 + Hg + NaCl = Hg_2Cl + NaO,SO_3$. In subliming calomel, it is an improvement to receive the vapour into hot water. This both tends to remove excess of corrosive sublimate, and condenses the salt in a finer powder. In any case, the sublimed calomel must be well washed to remove corrosive

sublimate, or calomel may be precipitated by decomposing nitrate of the suboxide with solution of chloride of sodium. Thus $Hg_2O,NO_5 + NaCl = HgCl + NaO,NO_5$. But as it is difficult to have the nitrate of the suboxide without some nitrate of the red oxide or peroxide; there is always a risk, by this process, of obtaining some corrosive sublimate. If calomel, therefore, is obtained in this way, it should be well washed. Calomel, when slowly sublimed, is found in four-sided prisms terminated by four-sided faces. It is almost quite insoluble in water. When calomel is exposed to the vapour of ammonia, it absorbs it and becomes black, and loses the ammonia again, and becomes black when exposed to the air. When digested in liquid ammonia it also becomes black, and there is formed a compound of suboxide and sub-chloride of mercury.

CHLORIDE, *Corrosive Sublimate, Oxymuriate of Mercury*, $Hg,Cl$ Eq. 136·2, is, like the subchloride, prepared in several ways—for example, by the action of excess of chlorine on mercury, and boiling with water, and concentrating the solution, or by dissolving the red oxide in muriatic acid; but it is generally prepared by digesting four parts of mercury with five of sulphuric acid, with the aid of heat, and evaporating until a mass of sulphate of mercury is obtained. The process has been already referred to under the head of sulphurous acid. The sulphate of mercury is next triturated with an equal weight of chloride of sodium, and sublimed, The process is explained by the formula $HgO,SO_3 + NaCl = HgCl + NaO,SO_3$. The specific gravity of the chloride of mercury is 6·5; it melts at 509°, and is volatilised at a somewhat higher temperature. It is soluble in sixteen parts of cold and three of boiling water, and is soluble in from two to three parts of cold alcohol and ether. It generally crystallises in rhombic prisms. It is very soluble in muriatic and nitric acids. Solutions of potass and soda, *not in excess*, give brown precipitates of oxychlorides with it. (See the red oxide.) When ammonia is added to a solution of corrosive sublimate, a substance falls which is known as white precipitate, and which is a double chloride and amide of mercury. The theory of its formation is very simple—$2HgCl + 2NH_3 = HgCl,Hg,NH_2 + NH_3ClH$.

Chloride of mercury forms numerous double salts. It combines with chloride of potassium in several proportions. Here it is the acid, and it has all the properties of an acid, reddening litmus. In general it combines in this way with all the electro-positive chlorides, forming a numerous and distinct class of double salts. Its compound of this character with chloride of ammonium is termed *sal alembroth*.

Chloride of mercury combines with albumen, forming a compound regarding the nature of which there has been much dispute, but which is now believed to be a direct compound of corrosive sublimate and albumen;—hence albumen is the best antidote for corrosive sublimate. Analogous compounds are formed by this substance with other protein compounds, and probably with some of the immediate elements of the vegetable tissues. It is owing to this that it possesses the power of preserving organic matters from putrefaction.

## BROMIDE OF MERCURY, HgBr2,

Is easily prepared by the direct action of bromine and mercury. It is only necessary to agitate the two together in water, and, to complete the process, apply a gentle heat. It is a white salt, in every respect analogous to the chloride. The subromide is altogether analogous to calomel, and may be formed from the bromide as calomel from corrosive sublimate.

### IODIDES OF MERCURY.

THE SUBIODIDE, $Hg_2I$, may be easily obtained by triturating iodide and mercury together in the proper proportions. It is a dark olive powder, exceedingly like calomel in its properties. It may also be obtained by mixing together solutions of nitrate of the suboxide and of iodide of potassium. It then falls as a yellowish-green powder, which, however, is apt to be mixed with some of the iodide.

IODIDE OF MERCURY, $HgI$; Eq. 227·06. This substance may also be obtained by the direct action of its constituents, triturated together in the proper proportions, and then subliming the product. It becomes yellow when heated, and sublimes in rhomboidal plates of a beautiful yellow colour. These gradually become red, and the change may be produced at once by breaking them. Iodide of mercury is very little soluble in water, requiring 150 parts to dissolve it. It is more soluble in alcohol. It is analogous to corrosive sublimate. When dissolved to saturation in a hot solution of iodide of potassium, it is deposited on cooling in scarlet crystals.

### SULPHURET OF MERCURY, HgS (*Cinnabar Vermillion*),

Is obtained when sulphuretted hydrogen is passed through a solution of a salt of red oxide of mercury, or when such a salt is treated by a solution of an alkaline sulphuret.* It falls as a black precipitate. It is obtained usually by adding mercury to excess of fused sulphur in a crucible, stirring, after heating in a sand bath, to expel excess of sulphur, and subjecting the product to sublimation. It is obtained in a crystalline sublimate of a splendid colour. It may be obtained of this colour in the moist way by decomposing the salts of the red oxide by the *higher* alkaline sulphurets, and digesting the product, which is at first black, at a gentle heat. Cinnabar is not acted on by the ordinary acid, but is by aqua regia.

### CYANIDE OF MERCURY, $HgC_3$; Eq. 124·7;

Is most readily prepared by dissolving red oxide of mercury in a solution of hydrocyanic acid. The solution may be evaporated, and

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* When an alkaline sulphuret decomposes a subsalt of mercury, a subsulphuret of mercury is at first formed; but this soon passes into metallic mercury and the sulphuret.

the cyanide crystallises in square anhydrous prisms. This salt is analogous to corrosive sublimate, which it very much resembles. It is not decomposed by alkalies. Hydrochloric and hydrosulphuric acids decompose it with evolution of hydrocyanic acid.

### CARBONATES OF MERCURY.

These are obtained by the action of alkaline carbonates upon the nitrates of mercury, and correspond with them in composition; the precipitate thus formed from the neutral nitrate of the suboxide is white; that from the nitrate of the oxide of a pale red colour.

### NITRATES OF MERCURY.

Of these there are several. The *Neutral Nitrate of the Suboxide*, $Hg_2O,NO_5+2HO$, is formed by dissolving mercury in excess of cold nitric acid. It crystallises readily from the solution, in rhomboidal crystals. It is soluble in a small quantity of water; treated by a large quantity, it is decomposed, and a subsalt deposited of the formula $Hg_2NO_5$ $+2HO$. By digesting the black oxide in solution of the neutral nitrate, a *subnitrate* is formed, which crystallises in white rhombic prisms, and has the formula $3Hg_2O, NO_5+3$ $HO$. The *subnitrate*, like the neutral nitrate, is soluble in a little water, but, treated with a large quantity, it leaves behind a white powder, which, on being washed, turns yellow. This has the formula $2Hg_2O,NO_5+HO$. When dilute ammonia is added to the soluble nitrates, so as not entirely to neutralise the acid, a black precipitate is formed, called Hahnemann's soluble mercury. Its composition is $2Hg_2O,NO_5+NH_3$.

*Neutral Nitrate of Oxide of Mercury*, $HgO,NO_5$, exists in solution when solutions of chloride of mercury and nitrate of silver are mixed, chloride of silver and nitrate of mercury being formed; but it cannot be crystallised in the ordinary way. When mercury is dissolved in nitric acid with the aid of heat, a subnitrate of the red oxide crystallises from it in small deliquescent prisms, whose formula is $2HgO,NO_5+2HO$. This salt is decomposed by water, leaving a salt of the formula $3HgO,NO_5+HO$; and, by long-continued washing with boiling water, the nitric acid is removed, and the oxide left.*

*Sulphate of Mercury*, $HgO,SO_3$, is easily obtained by boiling mercury in excess of strong sulphuric acid, as we have seen. It crystallises in small deliquescent needles. When thrown into a large quantity of cold water it is decomposed, and a salt formed, known

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* In order to obtain the neutral nitrate in the crystallised form, the solution should be exposed to a refrigerating mixture, or evaporated in the vacuum of the air-pump. It is not stable when formed.

as turbith mineral—formula $3HgO,SO_3$—some sulphate being dissolved in excess of sulphuric acid.

## COMPOUNDS OF MERCURY WITH METALS CALLED AMALGAMS.

Mercury combines with a very large number of metals, and there are few, probably, that, under every possible circumstance, would entirely resist its action. For instance, iron and platinum, which are not generally supposed capable of uniting with it, have been made to do so; the former by the electrotype process, the latter presented to it in a state of very fine division. Many metals are capable of being entirely dissolved by it, as gold, silver, tin, &c. An amalgam with tin is used to silver mirrors.

## TESTS FOR MERCURY.

Few metals possess more decisive reagents than mercury, or more capable of easy application.

1st. The metal itself is recognised, even in small quantity, by the globular form it assumes when sublimed. The sublimate appears in the form of fine dew, when in small quantity on the sides of a tube; and, examined by a Stanhope lens, the drops can easily be recognised by their metallic appearance and spherical form, and can be made to run together. Mercury is precipitated from its solutions of salts in the metallic form, by the addition to them of solutions of protochloride of tin; after a time a dark-grey deposit is formed, which, when heated, yields metallic mercury. It may also be precipitated on gold from its solutions, by putting the gold in contact with iron or zinc into them. For instance, if a drop of corrosive sublimate be placed on a sovereign, and the point of a knife applied to it, a deposit of mercury will immediately take place on the gold. The actions of alkalies and their carbonates of the salts of the oxides have been spoken of, also those of sulphuretted hydrogen, and hydriodate of potass. These various reactions are sufficient to distinguish the mercurial salts. In cases of poisoning, when organic matters are present, the same kind of difficulties that were experienced with arsenic are found. But the processes are much facilitated from the circumstance of protochloride of tin separating the mercury from its solutions. In cases where this process does not seem applicable, the organic substances may be carefully carbonised with sulphuric acid or nitromuriatic, and then tested nearly as Reinsch's test is applied for arsenic. Copper precipitates mercury as it does arsenic, and the heated copper gives a mercurial sublimate.

## 56.  SILVER, Ag (Argentum).

Eq. 108; sp. gr. 105; melts at 1873°.  Silver is found native, and also in the form of sulphuret, chloride, and carbonate, in various ores, along with gold, lead, copper, antimony, and arsenic.  It is obtained from its other ores, except lead, by amalgamation.  For this purpose, if the ore be in a native state, all that is necessary is to triturate it with a large quantity of mercury; the excess of mercury is poured off, the amalgam strained through leather, and the mercury separated by distillation.  If the metal be associated with gold, the gold will be removed by the same means.  The mode of separating the two metals will be described under gold.  In the amalgamation of the other ores which do not contain lead, they are first triturated with water and dried, common salt and sulphate of copper are added and triturated with the ore, then mercury is repeatedly triturated with it.  The amalgam is separated and distilled.  It appears that, in this process, in the first place, the chloride of sodium and sulphate of copper decompose each other, and chloride of copper and sulphate of soda are formed afterwards; the chloride of copper and sulphuret of silver, if that ore be present, are converted into chloride of silver and sulphuret of copper; while the silver dissolves in excess of common salt, and is reduced by the mercury with formation of calomel; or the sulphuret is roasted in a reverberatory furnace with common salt, so as to convert it into chloride.  It is then put into barrels with water, iron, and mercury, and these barrels made to revolve.  The silver is reduced by the iron, which takes its chlorine, and an amalgam is readily formed with the mercury.

Pure silver for chemical purposes is most easily obtained by dissolving impure silver, the most general alloy of which is copper, in nitric acid, and throwing down the chloride by the addition of solution of muriate of soda.  The chloride is to be washed and dried, and thrown into a crucible containing twice as much carbonate of potass at a bright red heat.  The silver is reduced, and chloride of potassium formed.  The heat is then to be raised to fuse the silver.  In the ordinary mode of separating silver from the common metals, called assaying, the alloy is melted with a large quantity of lead, and heated on a bone earth cupel in a muffle,* which allows access of air to the heated metal.  The lead is thus oxidated, and as the oxide produced is very fusible, it is absorbed by the porous bone earth cupel; the oxidation of the lead favours the oxidation of the copper.  In this way the more oxidable metal is removed, and at length a round button of pure silver remains.  Melted silver has the power of absorbing oxygen from the air; this oxygen it gives out on cooling, causing the surface of the metal to become blistered.

Silver may be obtained by dissolving neutral nitrate of silver in water, and inserting a piece of clean copper in the solution.  The

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* A muffle is a contrivance for heating a cupel in a furnace so as to secure the access of the air to it.

silver is deposited in a crystalline powder.   In the melted state
silver crystallises in cubes and octohedrons.   Silver is more malle-
able and ductile than any other metal, except gold.   The tarnishing
of silver in the open air is owing to the action of sulphuretted
hydrogen on it, which gas acts most rapidly upon it.   Silver is now
considered to form three compounds with oxygen.

### OXIDES OF SILVER.

These are the Suboxide, $Ag_2O$ ; the Oxide, $AgO$ ; and the Binoxide,
$AgO_2$.

The SUBOXIDE is prepared by heating the citrate of silver in a
current of hydrogen; one atom of oxygen is abstracted from two
atoms of the oxide in combination with the citric acid, and a citrate of
the suboxide formed.   The citrate of the suboxide is soluble in water,
and potassa throws down a black suboxide from the solution.   It is a
very unstable body, readily giving off oxygen, and leaving metallic
silver.

OXIDE OF SILVER, $AgO$, Eq. 116, is readily procured by the
action of solution of potassa on nitrate of silver.   It is precipitated
in the form of hydrate of a brown colour, which, washed and
dried, is of a darker hue.   The powder is anhydrous.   It is
slightly soluble in distilled water.   Its salts are isomorphous with
those of soda.   They are all decomposed by sulphuretted hydrogen,
yielding a black precipitate.   The oxide is soluble in ammonia.   The
soluble salts all give a white precipitate with chlorine, muriatic acid,
or muriate of soda, and besides afford precipitates with many other
bodies.   When fresh precipitated oxide of silver is left for some hours
in a strong solution of ammonia, the greater part is dissolved, but
there remains a dark substance, which, pressed when wet with a hard
body, or slightly touched when dry, vehemently explodes.   The com-
pound may be regarded as $AgO+NH_3$, or $AgNH_2+HO$, and the
explosion may be owing either to the liberation of amidogen itself, or
some decomposition whereby hydrogen is removed by the oxygen of
the oxide of silver, and the silver reduced.   This substance is called
*fulminating silver*, and is not the only explosive compound of the
oxide.

BINOXIDE OR PEROXIDE OF SILVER, $AgO_2$, is formed when a
dilute solution of nitrate of silver is decomposed by galvanism, crys-
talline needles of the peroxide forming at the positive pole.

### CHLORIDE OF SILVER, $AgCl$; Eq. 143·5.

This most important compound occurs in nature in cubes, and is easily
obtained by the action of a soluble muriate, or muriatic acid, upon solution
of the nitrate. The precipitate should be well washed and dried, secluded
from the light, which causes some decomposition of it, with escape of
chlorine.   Chloride of silver is perfectly insoluble in water, soluble in
ammonia, and by boiling in strong hydrochloric acid.   It melts at
about 500°.   Dry chloride of silver absorbs ammonia.   When boiled

in solutions of the alkaline chlorides, it forms double salts, which crystallise on cooling. The importance of this salt arises in great part from its use in estimating chlorine; for this purpose the chloride is fused in a platinum crucible.

### BROMIDE OF SILVER, AgBr, and IODIDE OF SILVER, AgI,

Are obtained by the action of an alkaline hydrobromate or hydriodate, or the hydracids of the respective elements, on solution of the nitrate of silver. They closely resemble the chloride, from which, however, they are easily distinguished by heating them in an atmosphere of chlorine, or in a test tube, with a little chloride of lime, bleaching powder, and muriatic acid. Under these circumstances the red vapours of bromine and the purple vapours of iodine are respectively disengaged.

### CYANIDE OF SILVER, AgCy,

Is prepared by the action of hydrocyanic acid, or an alkaline cyanide, on a solution of nitrate of silver. It resembles very much the chloride, bromide, and iodide, from which it is distinguished by its solution in boiling nitric acid, and by giving off cyanogen when the dried cyanide is heated. The cyanide should be heated in a tube having a bulb at the closed extremity, in which the cyanide is placed; the tube should be drawn out at the other extremity to a fine point, and the stream of cyanogen disengaged, inflamed.

### SULPHURET OF SILVER, AgS,

May be obtained by heating strongly sulphur and silver. It fuses at a high temperature, and, on cooling, forms a dark, soft crystalline mass. It is also obtained as a black precipitate. A solution of a salt of silver treated with sulphuretted or an alkaline sulphuret yields it.

#### SALTS OF OXIDE OF SILVER.

*Carbonate of Oxide of Silver*, $AgO,CO_2$, is obtained by the action of an alkaline carbonate on solution of nitrate of silver. It is white, and insoluble in water—soluble in nitric acid, with effervescence.

*Nitrate of Silver*, $AgO,NO_5$, Eq. 170, is readily obtained for common use by the action of nitric acid on silver, slightly assisted by heat. As the ordinary silver coin contains a fraction more than one-twelfth of its weight of copper, the nitrate of silver so prepared, although sufficiently pure for ordinary purposes, is anything but chemically pure. The solution so obtained can be precipitated, if it is desirable, with chloride of sodium, and pure silver obtained from the chloride as already described, from which a pure nitrate can be obtained. Nitrate of silver crystallises from a hot saturated solution in beautiful, almost transparent, white tables, which, on being exposed to the air and light for some time, become darkened at the edges. It is soluble in its own weight of hot, and four parts of cold water, and in alcohol. When the dry salt is heated, it melts, and

can be run into moulds, when it forms the stick used as *lunar caustic.*
A solution of nitrate of silver readily indicates the presence of organic
matter, becoming dark, and yielding a reddish-brown precipitate—a
compound of the organic matter and oxide of silver.   To its power of
forming a similar compound with albumen it owes its uses as a caustic.
Its reduction by organic matter, and the subsequent blackening by
light, is the cause of its being used as the basis of marking inks.

*Sulphate of Silver,* $AgO,SO_3$, Eq. 156·0, is procured either
by acting on silver with concentrated sulphuric acid, with the aid of
heat, or by decomposing nitrate of silver by sulphate of potass.   From
a hot solution it is deposited in anhydrous crystals.   It is soluble
in about ninety parts of water, at 212°.   Both this salt and the
nitrate combine with ammonia, by which the sulphate is rendered very
soluble in the ammoniacal solution, from which, by evaporation,
crystals may be obtained, containing eqs. $AgO,SO_3$ and $2NH_3$.

*Hyposulphite of Silver,* $AgO,S_2O_2$.   This salt is obtained as a
white precipitate when nitrate of silver in solution is acted upon
by an alkaline hyposulphite.   When oxide, chloride, iodide, or
bromide of silver is treated by a solution of hyposulphite of soda,
it is dissolved—a hyposulphite of silver is formed, which is soluble
in excess of solution of the alkaline hyposulphite.   It is in this
way, as has been partly explained, that the hyposulphite is used
to remove excess of the salt of silver in the photographic process,
which, if remaining, would continue to receive impressions from
objects destroying the original picture.

### TESTS FOR SILVER.

The precipitates which nitrate of silver yields with reagents,
and which closely resemble each other, are the carbonate, chloride,
bromide, iodide, cyanide, oxalate, citrate, and tartrate.   The chloride,
bromide, iodide, and cyanide, may be distinguished as described.
The carbonate dissolves in $NO_5$, with effervescence.   The pre-
cipitates with the vegetable acids are distinguished from the
rest by being all reduced by heat.   The best way of testing them
is to collect them on a filter, dry them, and then heating the
filter gently over a spirit lamp, so that it may not catch fire.   The
oxalate fulminates faintly, and is dispersed; the citrate, when heated,
becomes quite brown, froths up, and then deflagrates, giving off white
fumes, and leaving an abundant grey pulverulent residue, which, on
the further application of heat, becomes white, and is pure silver.   The
tartrate becomes brown, and froths but does not deflagrate, gives off
white fumes, and leaves a botryoidal mass, which, on being heated to
redness, likewise becomes pure silver.

## 57.  GOLD, Au (Aurum).

Eq. 98·33; sp. gr. from 19·4 to 19·65.  It occurs native, and associated with other metals.  It is separated by mechanical means— crushing and washing, or by these assisted with amalgamation.  It is separated from silver by nitric acid; and as, when the silver is in small quantity, it resists the action of nitric acid, an operation called *quartation* is then employed.  One part of the alloy is fused with four parts of silver, when the whole silver may be dissolved by nitric acid.  Pure gold may be obtained by precipitating a solution of chloride of gold-made acid by hydrochloric acid with protosulphate of iron.  The gold is thrown down as an orange-coloured powder.  Pure gold is the most malleable and ductile of all the metals.  It melts at 2016°, and contracts when it becomes solid.  It can be oxidated by heating it with several fluxes. Its great solvent is the *aqua regia*, already described (see p. 42).  It forms two oxides—$Au_2O$, and $Au_2O_3$; but as the equivalent of gold is sometimes doubled, these oxides are then represented as $AuO$ and $AuO_3$.

### Suboxide of Gold, $Au_2O$; Eq. 204·66;

Is obtained by decomposing the subchloride by a dilute solution of potassia.  Muriatic acid decomposes it, forming a solution of the sesquichloride, and leaving some gold.  This oxide is readily reduced by heat. The purple of Cassius is supposed to be a compound of one eq. of this oxide with two eqs. of the peroxide and one of the protoxide of tin. It may be prepared by the addition of a solution of the protochloride of tin to a dilute solution of chloride of gold.  It is obtained by several other modes.  Its exact composition is doubtful.  When heated, it becomes peroxide of tin and metallic gold.  Its principal use is in giving a fine purple-red colour in staining glass and porcelain.

### Sesquioxide of Gold (*Teroxide of Gold*), $Au_2O_3$; Eq. 220·66;

Is prepared by digesting a solution of the sesquichloride of gold with magnesia.  In this way a precipitate of the sesquioxide and magnesia is formed, which should be collected on a filter, well washed, and boiled with nitric acid, which dissolves the magnesia, and leaves the sesquioxide in the form of a hydrate.  This oxide is soluble in muriatic acid, becoming the sesquichloride, soluble in some other acids, but insoluble in water.  Hydrogen or carbon reduces it at a moderate temperature; it is also reduced below redness.  It is called also auric acid, having the power of forming compounds with alkalies, acting as the acid.  The most remarkable of these is the aurate of ammonia, or fulminating gold.  This is prepared by digesting the sesquioxide with solution of ammonia; a dark powder is formed, which should be carefully dried.  It explodes when rubbed or slightly heated.

SUBCHLORIDE OF GOLD, AuCl; SESQUICHLORIDE (or *Perchloride*), $Au_2Cl_3$; Eq. 303·16.

The first of these compounds is prepared by simply evaporating a solution of the perchloride or sesquichloride to dryness. A high temperature decomposes it, metallic gold and the sesquichloride being formed. The second body, the most important of all the compounds of gold, is obtained by the solution of the metal in aqua regia, or when the subchloride is exposed for a considerable time to the action of water. The water acts on the subchloride in much the same way as heat, and causes it gradually to pass into the perchloride and metallic gold. On evaporating a solution of gold in aqua regia by means of a water bath, a brownish crystalline deliquescent mass is left. On exposing a strong solution of the sesquichloride to cold, a similar mass is obtained. The perchloride is very soluble in alcohol or ether. It is easily decomposed by heat; carbon, and especially phosphorus, precipitate metallic gold from it. Almost all the metals have the same action. Sesquichloride of gold forms double salts with alkaline chlorides.

### SULPHURETS OF GOLD.

When sulphuretted hydrogen is passed into a hot solution of the sesquichloride, a dark-brown precipitate or subsulphuret is formed; when into a cold solution of the same salt, a black sesquisulphuret is the result.

Gold is recognised by the properties of its salts already described, and by the action of solution of bromide of potassium in solution of its chloride. The result is a dark splendid brown hue, due to the formation of bromide of gold.

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SECT. 9.—METALS FOUND WITH NATIVE PLATINUM.—These are, Platinum, Palladium, Iridium, Osmium, Rhodium, and Ruthenium.

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## 58. PLATINUM, Pt.

Eq. 98·68, sp. g. 21·63. Is always found native, generally in small grains, associated with gold, silver, iron, copper, and the above-named metals. When it contains gold and silver, these are separated by amalgamation; the ore is then dissolved in aqua regia. The platinum is dissolved, and the greater part of the iridium and osmium left behind. The solution is concentrated, and muriate of ammonia added, which throws down the platinum, and some iridium, as chlorides in combination with chloride of ammonium. A little platinum still remains in the solution, which is obtained by precipitation with metallic iron solution of the precipitate in aqua regia, and fresh precipitation by

chloride of ammonium ; the double chloride is then washed and ignited, a spongy mass of platinum is the result, which, by repeated pressure and heating, is at last obtained in the malleable form. Platinum is very malleable, and in ductility is inferior only to gold and silver. It is also very tenacious. Platinum may be softened, but cannot be melted in the strongest blast furnace. It is easily melted by the heat of the oxyhydrogen blowpipe ; and may even be volatilised. It resists the action of every single acid. These properties render it extremely useful in chemistry and the arts. There are three forms in which platinum is known—the malleable, and spongy platinum, and platinum black. The power which platinum possesses of causing the combination of oxygen and hydrogen, it shares with its allied metals.

The spongy platinum may be prepared by igniting the chloride of platinum and ammonium. The powder called platinum black is prepared by dissolving the protochloride of platinum, with the aid of heat, in a concentrated solution of potass ; successive portions of alcohol are then added, and the liquid stirred. Great effervescence takes place, carbonic acid being disengaged, and a black powder thrown down. This powder is boiled with alcohol, muriatic acid, and potass successively ; and then with water. It is a black powder, resembling soot. It absorbs and condenses gases like charcoal, and is the form in which platinum most readily brings about the combination of gases. The readiest solvent of platinum is aqua regia. It is acted upon by the caustic alkalies in a state of fusion ; also by phosphorus and arsenic. This, of course, suggests certain precautions in the use of platinum vessels. There are two oxides of platinum—$PtO$, and $PtO_2$.

### Protoxide of Platinum, $PtO$ ; Eq. 106·68.

It is obtained by decomposing the protochloride with potassa. It is a black powder—a hydrate. When just precipitated, it is soluble in excess of the alkali. When the hydrate is heated it loses both water and oxygen, forming metallic platinum. It forms a class of salts called platinous. These are distinguished from the salts of the peroxide by not giving precipitates with sal-ammoniac. They have a greenish-brown hue in solution, and are formed by dissolving the oxide in various acids. When heated with muriatic acid, the protoxide forms a solution of the bichloride, and metallic platinum is thrown down.

### Binoxide or Peroxide of Platinum, $PtO_2$, Eq. 114·68,

Is obtained in the state of a hydrate, containing two atoms of water, when solutions of the bichloride and potassa, the latter in excess, are mixed. At first a double chloride of potassium and platinum is precipitated, which re-dissolves on the mixture being heated, forming a platinate of potass. On treating this with acetic acid in excess, the peroxide is thrown down. When this hydrate is heated it loses water, and then its oxygen, leaving metallic platinum. It combines with both acids and alkalies, acting both as a base and an acid. Thus it is

soluble in nitric acid, and by the action of nitric and sulphuric acids upon the sulphuret a sulphate can be formed. On the other hand, the hydrate is soluble in alkaline solutions, forming platinates. Its salts are of a brown colour.

PROTOCHLORIDE OF PLATINUM, PtCl, Eq. 134·18; BICHLORIDE OF PLATINUM, PtCl$_2$, Eq. 169·68.

The former of these bodies is obtained by evaporating a solution of the latter in a sand bath, at a temperature not exceeding 400°, as long as it gives off fumes of chlorine. The residue is a greyish green powder, quite insoluble in water. It is acted upon by hydrochloric acid, which first dissolves it, and then gradually forms the bichloride, and leaves metallic platinum. The bichloride is procured by dissolving metallic platinum in aqua regia, and evaporating till a syrupy mass is obtained. This should be dissolved in muriatic acid, and again concentrated. It is a brown non-crystallisable body, exceedingly deliquescent. Its solution is yellow. It is soluble in alcohol. A solution of it in this fluid is employed to separate and estimate potass in analyses. It throws down potass from its salts, as a double chloride of platinum and potassium, of which 100 grains contain 19·33 of potass.

A green salt, a compound of ammonia and protochloride separates gradually in a crystalline form, when a solution of ammonia is added to the double chloride of platinum and ammonia.

The hydriodate of potass gives a very dark colour when added to a solution of the chloride of platinum. More than one sulphuret may be formed.

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## 59. PALLADIUM, Pd.

Eq. 53·27, sp. gr. 11·5, is precipitated from the mother liquid after the separation of platinum, by chloride of ammonium, principally by the action of cyanide of mercury, whereby the cyanide of palladium is thrown down, which, being ignited, leaves spongy palladium capable of being made malleable in the same way as platinum. Palladium closely resembles platinum in its properties, but is somewhat intermediate between it and silver; thus it is dissolved by nitric acid, but is not, like silver, tarnished in the air by sulphuretted hydrogen.

The remaining metals of this group are so little likely to come under observation, that they may be omitted from a work like the present.

# PART IV.

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## ANALYSIS OF MINERAL WATERS.

As an exercise of analytical chemistry, the student cannot do better than take the analysis of a mineral water as a beginning.

The analysis of a water divides itself—1st, into its qualitative, and 2nd, its quantitative analysis. By the former process we learn its physical qualities, and the nature of its ingredients; by the latter, the quantities in which these ingredients exist.

The first point in the qualitative analysis is to ascertain the density of the water. This is best done by weighing it in a compensated bottle, holding at 60° exactly 1,000 grains of distilled water. The difference in weight will give some idea of the amount of solid matter held in suspense or solution in the water, although a very precise formula for that cannot be given. The water of the British Channel, which has a sp. gr. of 1027·4, contains 35·253 of solid matter in 1,000 parts.

Then it should be ascertained whether the water is acid or alkaline by means of test paper, and whether it belong to one of the five following classes of mineral waters, viz : carbonated—i. e. containing excess of carbonic acid ; sulphureons—sulphuretted hydrogen ; saline— excess of neutral salts ; alkaline—containing carbonate of soda ; or chalybeate—containing iron.

Free carbonic acid is determined by litmus paper, which, if it be reddened before the water is boiled, and not afterwards, and the colour disappears on warming the test paper, indicates the presence of this gas. Sulphuretted hydrogen is readily ascertained by solution of sugar of lead ; carbonate of soda is indicated by the water affecting reddened litmus after boiling ; the presence of iron is best indicated by adding a drop of nitro-muriatic acid, and testing with an infusion of gall, or by suspending a chip of nutgall by a string in the liquid exposed to air for a few hours. If the liquid, without possessing any of these characters in excess, on being evaporated leaves a considerable residuum of neutral salts, it is called a saline water.

Other general qualities of the water may be ascertained before proceeding to minute particulars ; as, whether it contains much organic matter by the addition of solution of nitrate of silver, which soon gives a reddish-purple precipitate with organic matter ; and its hardness. The latter quality is estimated by the soap test of Dr. Clark.

For the purpose of this test, in the first place 16 grains of neutral chloride of calcium (prepared by solution of carbonate of lime in muriatic acid, and repeated evaporation to dryness, and re-solution and evaporation in an air-bath until all the excess of acid is driven off) are dissolved in a gallon of distilled water, which is then said to be of the sixteenth degree of hardness, and a soap solution is formed by dissolving 120 grains of Hawes' white curd soap in a pint of proof spirit. The former of these liquids is used to graduate the latter. An apparatus graduated like fig. 28 is employed, each of the 100 measures being equal to ten grains of distilled water. One hundred measures of the solution are put into a stopper bottle capable of holding twice the quantity of water. The soap solution is carefully added, and the bottle with the stopper is agitated from time to time, and the soap solution added, until the lather which is formed remains for five minutes on the surface of the liquid. This process is carried on until it is ascertained, by adding more soap or more spirit to the soap solution, that 32 measures of it will neutralise 100 measures of water of 16° of hardness.

In testing the water, it is first violently agitated in a stoppered bottle, to get rid of any carbonic acid it may contain, and the air disengaged is sucked out, and this is done until it is supposed to be free of carbonic acid. The soap solution is then added to 100 measures of it in a stoppered bottle, and the mixture treated as above described, and the hardness estimated from the number of measures of soap solution required to cause a permanent lather to be formed, according to the subjoined table:

| DEGREES OF HARDNESS. | MEASURES OF TEST SOAP SOLUTION. |
|---|---|
| 0° | 1·4 |
| 1 | 3·2 |
| 2 | 5·4 |
| 3 | 7·6 |
| 4 | 9·6 |
| 5 | 11·6 |
| 6 | 13·6 |
| 7 | 15·6 |
| 8 | 17·5 |
| 9 | 19·4 |
| 10 | 21·3 |
| 11 | 23·1 |
| 12 | 24·9 |
| 13 | 26·7 |
| 14 | 28·5 |
| 15 | 30·3 |
| 16 | 32·0 |

When the water is so hard that it will not yield a permanent lather with 32 measures of the soap solution, it must be diluted with an equal bulk of distilled water, and the solution of soap applied as before; and

the process must be carried on till 60 measures of the soap solution have been used. If no result be still obtained, other 100 measures of water must be added, and the soap solution added till 90 measures of it have been used; then the number of soap measures used must be divided by the number of 100 measures in the mixture, and the quotient placed opposite the number of degrees in the table. Finally, this must be multiplied by the same division for the true number of degrees of hardness. The number of degrees of hardness nearly corresponds to the quantity of carbonate of lime reckoned in grains, *equivalent* to the lime, magnesia, alumina, and iron in the gallon of the water, reckoning the hardness by grains corresponding to the degrees.

The qualitative analysis of the water is then to be divided into that of its solids and its gases. The former should be first sought for, except when the quantity of water that can be obtained is small, and it is desirable to analyse for the gases. In general, the estimate of the solids is alone cared for, and that of carbonic acid gas, or sulphuretted hydrogen. The first point in the analysis for solids is to determine what bases exist. These are almost always potassa, soda, lime, magnesia, alumina, and iron.

It is first well to test the water, with the exceptions below, before boiling or any other operation has been performed. Portions of it, of about the same quantity, a couple of ounces, may be poured into six or eight test glasses.

The detection of potass or soda in solution, in the unconcentrated water, is hardly to be expected. For this purpose, it is best to boil down a quantity of the water, in proportion to its supposed strength, but not less than a quart, to dissolve the residue in a little water, and divide it into two portions; a drop or two of muriatic acid is to be added to one of them, and then a little of the bichloride of platinum. If a yellow lemon precipitate is formed, it should be collected, and washed with alcohol. The other may be again evaporated to dryness, and a portion of the residue exposed on a platinum wire to the reducing or inner flame of the blowpipe. If it give a yellow colour to the outer flame, soda may be concluded to be present.

With regard to the remaining earthy bases, lime, magnesia, and alumina, the best mode of proceeding is to add a slight excess of ammonia to a portion of the water, and to leave the precipitate, if any, to subside in a stoppered bottle. In this way is thrown down alumina; but, if the water contains excess of carbonic acid, it may throw down the carbonates of lime and magnesia. The liquid, if excess of carbonic acid be present, should be gently heated for some time; then the ammonia may also throw down magnesia. To prevent this, a little hydrochloric acid should be added to the liquid before the addition of ammonia. The precipitate by ammonia may also contain iron. This will be recognised by its colour. To the ammoniacal liquid separated from its alumina by filtration, a solution of oxalate of potass is to be added, which produces a precipitate when lime also is present in the water. After this precipitate has been removed, the addition of phos-

phate of soda will cause a precipitate if magnesia exists in the water. The presence of iron is readily known by the addition of its tests already described, or by the addition of hydrosulphate of ammonia, which gives a dark precipitate with it, as with other metals.*

The next point is to determine what acids may exist in combination with the bases. These will generally be the sulphuric, muriatic, carbonic, and hydrosulphuric; more rarely, the phosphoric, nitric, hydrofluoric, and silicic (if we consider it an acid, and not a base).

The water is to be put into test glasses as before. A certain portion is to be rendered acid by the addition of muriatic acid, to which a solution of muriate of baryta is to be added; if it contains sulphuric acid a precipitate will be produced insoluble in all the dilute acids.

To another portion of the water a little nitric acid is added, and then a solution of nitrate of silver. If the mineral water contains sulphuretted hydrogen, or a soluble alkaline hydro-sulphate, a solution of the sulphate of copper should first be added; thus the sulphur is all precipitated as sulphuret of copper, which is gradually deposited at the end of a short time. It is to be collected on a filter, the filtered liquid is then to be treated, at first with a little nitric acid, and then with solution of nitrate of silver, which throws down the chloride of silver if muriatic acid (a muriate or chloride) exists in the liquid. Of course a bromide or iodide would be thrown down in the same way.

Another portion, quite fresh from the spring, is treated with lime water, which gives a precipitate when the water contains carbonic acid. The presence of this acid is also generally known by the appearance of the water. The difference between the precipitate which lime water will sometimes produce with waters containing free carbonic acid, and those containing an alkaline carbonate, is known by the precipitate being dissolved in excess of the former, and not in that of the latter.

The presence of hydrosulphuric acid is readily indicated by its smell, and its action on metallic salts, giving a dark precipitate with solutions of nitrate of silver and acetate of lead.

Phosphoric and hydrofluoric acids with lime, in the form of phosphate and hydrofluate, exist in very small quantity in mineral waters, and in those in which they exist are held in solution by excess of carbonic acid. The ordinary tests for phosphoric acid are seldom applicable. The water can be concentrated to 1-16th, and the precipitate which falls treated in a platinum crucible with muriatic acid, until any carbonic acid present is driven off, and a former carbonate converted into a muriate. The solution is saturated with ammonia in a stoppered bottle, and the clear liquid decanted, after the whole has stood some time, from the precipitate, which is to be collected on a filter, washed, dried, and heated in a platinum crucible with strong sulphuric acid. The top of the crucible is to be covered with a glass plate, covered with a layer of wax, having characters cut on it. If, on removing the wax, these are acted upon by the fumes which have been disengaged, a hydrofluate

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* Of course many other bases may, in rare cases, exist in greater or more minute quantities.

was present. The residue in the crucible may then be treated with boiling water, and precipitated by the addition of muriate of baryta, and the precipitate treated with muriatic acid; by the former addition, sulphate and phosphate of baryta are thrown down; and by the latter, the phosphate is re-dissolved. The solution is to be treated by acetate of potassa in excess, which causes the muriatic acid to be replaced by the acetic. Solution of sesquichloride of iron, is then added. If a white, gelatinous precipitate be produced, phosphoric acid is present.

Silicic acid is ascertained to be present by evaporating to dryness, and treating the precipitate for some time, say twenty minutes, with a little muriatic acid—little more, in fact, than is sufficient to well moisten it. It is then to be treated with water; what remains must then be dried, and examined with the blowpipe. It is thus recognised whether silica is present in any quantity: first, by fusing the mass with a salt of phosphoric acid, when a bead of silica will be left infusible in the fused mass. Secondly, by fusing it with carbonate of soda, when it will dissolve with effervescence, and from a glass. If the silica, as is generally the case, be in very small quantity, the best plan is to concentrate the water, as above described, to a 1-16th, and treat the precipitate then formed as described.

Nitric acid when present is supposed to proceed from organic decomposition. It is frequently found in the well-water of towns. In order to obtain indications of it, the water should be very much concentrated, then the solution separated from the residuum, treated with strong sulphuric acid, and a crystal of the green sulphate of iron put into it. If nitric acid be present, the iron will be peroxidised, and a red hue produced.

The gases present in mineral waters besides sulphuretted hydrogen and carbonic acid, are generally oxygen, nitrogen, and very rarely carburetted hydrogen (very rarely hydrogen). In order to ascertain the presence of these, a retort must be taken and measured, and a safety tube inserted into it; a given quantity of the water is then to be introduced, filling the retort, or nearly so. The water is then to be heated, and the expelled gases passed into a solution of acetate of lead with excess of acetic acid added to it,* and then through lime water. Such an apparatus as is known by the name of Woulfe may be used. The sulphuretted hydrogen is absorbed by the former, and the carbonic acid by the latter; the gases which escape are collected over mercury. Some idea of their nature may be obtained by their quantity. If not exceeding in that respect the amount of air expelled so near as can be calculated from the flask, then the presumption is that nothing but atmospheric air is present. If the quantity collected exceed that, it may be divided into two or more portions for examination. If the gas does not support combustion, and is not inflammable, then it is azote; if it supports combustion more brilliantly than air, then it is in whole or in part oxygen; and if it burns, it is hydrogen, or carburetted

* This is to prevent precipitation of carbonate of lead, and a mixture of carbonate and hydrosulphate of lead being formed.

hydrogen. The former burns with a feeble bluish flame, and if mixed over water with an equal volume of chlorine, and exposed to daylight, it is gradually converted into muriatic acid, which is absorbed; while the carburetted hydrogen burns with a brilliant flame, and if mixed with an equal volume of chlorine over water, it is absorbed, and there appear on the surface little drops of oil, while the water acquires an ethereal odour.

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### QUANTITATIVE ANALYSIS.

It is to be observed that a qualitative analysis gives no idea of the mode of combination in which the constituents of a mineral water exist; it merely shows their presence. When it is known that a water contains such and such acids, and such and such bases, we are still at a loss to know how these are combined; and the rule observed is to place the strongest acids in combination with the strongest bases: thus we should rather assign sulphuric acid to the alkalies, than to the earths existing in the same water. After the existence of so much acid is known, we should first give as much of it as was required to saturate the alkaline bases, and then give the remainder to the earths, taking them in the order in which they have been ranked in this and other works.

The quantitative analysis of a mineral water is of much more difficult execution, and to go into its details would exceed the limits of this work. The subject of chemical analysis *generally* is beyond these, and therefore to treat fully of the subject of the analysis of mineral waters would require details to a much greater extent than would be required in a work on analytical chemistry, in which the general rules for analysis being given, those for mineral waters would partly come under such general heads.

The total amount of solids in a mineral water is readily ascertained. About a pint of the water, if it be moderately strong, is evaporated to dryness slowly in a porcelain dish, covered with a paper funnel, and transferred by degrees to a weighed platinum vessel, in which it is evaporated to dryness by means of hot air. The weight gives that of the whole solids. The dish is then heated more strongly, so as to calcine all the organic matter, the quantity of which is represented by the loss sustained.

Half a gallon of the water may be evaporated in a similar way with a few drops of nitric acid. The residue is to be treated with dilute muriatic acid, which dissolves other bases, and leaves silica, which can be weighed. The solutions and the washings of the residue (which is to be collected on a filter, well washed, and being ignited with the filter to be weighed) are then to be treated with ammonia, which throws down the alumina and iron: these are to be collected on a filter, washed, ignited, and weighed. The lime is to be thrown down from the residual solutions as oxalate, by means of solution of oxalate of ammonia. The precipitate is collected on a filter, washed, and

dried; it is then incinerated with the filter: the result is then treated with a little strong solution of common carbonate of ammonia, dried in an air-bath and weighed. The result is carbonate of lime.

The residual filtered solution and washings are then treated with solution of chloride of ammonium (muriate of ammonia), and excess of solution of phosphate of soda added. The mixture is then well stirred, and set aside for several hours. The precipitate is collected on a filter, and washed with water containing a little ammonia. The precipitate dried and ignited is pyrophosphate of magnesia.

The mixed precipitate of alumina and iron having been weighed, is dissolved in dilute muriatic acid. It is then heated in a silver vessel with solution of pure potass, and the precipitate washed with hot water dissolved again in muriatic acid, thrown down by ammonia, washed, dried, and ignited. It is the peroxide of iron which probably existed as protoxide in the water. The residual solution, after the iron was precipitated by the potassa, treated with ammonia, gives the alumina.

To determine the potassa and soda, a quart or two of the water is to be concentrated by evaporation till its bulk is reduced by 4-5ths, then treated with solution of chloride of barium and baryta; the solution is then to be heated, and separated by filtration from the precipitate. The solution and washings of the filter are evaporated and greatly concentrated, then treated with ammonia and carbonate of ammonia, to separate any excess of baryta, heated to dryness in a weighed dish, and then the residue weighed. It is composed of chloride of potassium and sodium. The residue is dissolved, and mixed with a little muriatic acid and bichloride of platinum; the solution is evaporated to dryness, and treated with pure alcohol, which leaves undissolved the double chloride of potassium and platinum; the weight of this calculated gives the amount of potassium; and the amount of chloride of potassium taken from the residual chlorides of sodium and potassium, the amount of chloride of sodium.

The common acids present in water are easily determined quantitatively. The sulphuric and muriatic generally by the addition simply of chloride of barium and nitrate of silver. Carbonic acid should, if possible, be determined at the spring by introducing solution of chloride of calcium and ammonia into bottles of the water. The precipitates obtained from the bottles are mixed, and the whole collected on filters; the residual precipitates from the filters are ignited, and weighed both when just ignited and on cooling, and after some exposure to the air. Thus the amount of carbonic acid is ascertained.

A similar mode is followed for sulphuretted hydrogen, i.e. into bottles at the spring a little muriatic acid and solution of arsenious acid are introduced, and after some time the sulphuret of arsenic formed is collected and weighed.

Lastly, the amount of alkaline carbonates is determined by evaporating to dryness a quart or two of the water, collecting, washing, and drying the precipitate. This is then divided into two parts, both of which are weighed; the amount of muriatic acid in the one portion is then ascertained, the other is acidulated with muriatic acid, and the amount of

the same acid in this ascertained.    The difference between the two
will represent the amount of carbonates decomposed, by the difference
between the atomic weights of muriatic acid or chlorine and that of
the displaced carbonic acid.

In all these analyses the washing of the precipitates is a matter of
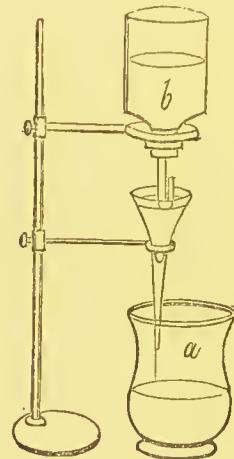


Fig. 36.                                      Fig. 37.*

great consequence.   For this purpose a washing apparatus like that
shown in fig. 36, termed a washing bottle, is used, or an apparatus like
that in fig. 37, which is contrived so as to allow of the gradual introduc-
tion of air into, and consequent displacement of water from, the upper
bottle.


* $a$ is the vessel receiving the washings ; $b$ the washing bottle, which
has a contrivance on one side of the tube for the gradual admission of air
into $b$.

# PART V.

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## ORGANIC CHEMISTRY.

BY Organic Chemistry is understood that portion of the science which relates to organised beings, both vegetable and animal. It is obvious that there might be two modes of treating such a subject. We might take every organised being, and make, as it were, a chemical dissection of it—an analysis, as we might do that of the constituents of the inorganic world, recognised as different by the senses; or we might treat of the elements of organic beings and their compounds, without reference to the mode in which they are combined or mixed in nature, but looking merely at their purely chemical nature and relations, as we have done in inorganic chemistry. But, looking at the various forms of organic nature, we shall find much more resemblance in their chemical composition than in mineral substances. Between, for instance, the sulphuret of iron and muriate of soda, there is not the least analogy, as they occur as ores in nature; but between the constitution of the dissimilar organised beings, as an ox and a man, a vegetable and an animal, there are exact or strong chemical resemblances.

In looking at the chemical constitution of organised beings, we find them to be composed—first, of certain principles called immediate, which exist in the tissues of vegetables and animals, such as we can obtain them from these sources by chemical analysis more or less complex, in some instances very simple; and secondly, of ultimate principles or elements, which in most instances can only be obtained by the destruction of the former. Sugar, starch, gluten, fibrin, albumen, are examples of the former; carbon, oxygen, hydrogen, and azote of the latter. To the study of these immediate principles, and their ultimate composition, perhaps the term *organic chemistry* may be properly applied, and again more properly still to the study of such of them which cannot be formed by artificial means, or without the intervention of life; for, looking attentively at these principles, some are to be found altogether identical with those which exist in inorganic nature, others peculiar, and requiring, as far as is yet known, the action of the power which is called *life* to produce them. Physiological disputes as to the nature of this power or force are immaterial here. It is enough for the chemist to recognise its existence, and its power to produce chemical combinations, which he cannot effect in the laboratory; he must, therefore, recognise its existence as he would

that of a simple body, viz., because he cannot decompose that body. As far as chemistry goes, this principle of life may be regarded as a catalytic force ; but the bodies formed by its influence are not the less proper objects of chemical study because their mode of formation is not understood.

Of these principles, then, some are precisely such as exist in the organic world, as water, muriate of soda, phosphate of lime ; others, like fibrin, starch, or gluten, are entirely of organic origin ; they cannot be made from the materials of the inorganic world, except through the intervention of life ; nor, as far as is yet known, can animals derive them from inorganic nature, except through the medium of vegetables.*

One great difference between organic and inorganic nature is the rare occurrence of elements *native* in the former ; except, perhaps, oxygen, hydrogen, and azote, no elements exist *as such* in organic bodies. Granting the existence of these three, they would be therefore both immediate and ultimate principles.

Organic chemistry, however, is generally understood in a much more extensive sense, viz. : as including not merely the study of the chemical principles which exist in the organic world as such, but also, not only their actions on each other, but the action of inorganic bodies on them, whence numerous compounds result, which do not in many instances exist in the tissue of organised beings.

For instance, sugar is obtained from vegetables or animals, and from sugar alcohol is procured by the catalytic action of a ferment, and by the action of acids on alcohol a whole class of bodies called ethers are produced, which do not exist in living beings, but are still studied under the head of organic.

The chief elementary constituents of organic bodies are carbon, oxygen, hydrogen, and azote ; but although these principles make up the greater part of their bulk, they contain several other elementary bodies, as sulphur, phosphorus, chlorine, bromine, iodine, potass, soda, lime, iron, &c. ; and perhaps there is hardly an elementary body which does not exist in greater or less quantity in organic nature. Carbon is a principal constituent of organic bodies ; but not the principal constituent of animals, the greater portion of whom is composed of water. But nearly all organic bodies contain a large quantity of carbon, and as this is united with more volatile and combustible compounds, or

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* The nearest approach yet made to the artificial formation of an immediate principle of the second class from inorganic materials, is in the formation of cyanide of potassium, as at p. 67. That of artificial urea from ferrocyanide of potassium and peroxide of manganese, so often quoted, is not a case in point, as the ferrocyanide was itself derived from an organic source ; but from the cyanide of potassium the other compounds of cyanogen can be derived. Such a process may furnish the key to the production of some kinds of food artifically—an object, the attainment of which would be quite as profitable as the philosopher's stone.

rather in compounds which, on being heated, are partly resolved into compounds very volatile and inflammable, of carbon, oxygen, and hydrogen, leaving a portion of the carbon at a moderate temperature, the process of *charring* is a test of organic matter.

Organic chemistry has been defined to be the chemistry of compound radicals; such bodies are more commonly found to exist, or presumed to exist, in organic chemistry; but we have spoken of amidogen, sulphion, &c.

The doctrine of compound radicals is, as has been seen, a modification of the chlorine doctrine. After muriate of soda, and analogous bodies, came to be looked upon as chlorides of metals, instead of muriates of oxides, the same simple view of the constitution of other salts began to be taken; and thus, instead of $KO,SO_3$, we had K, $SO_4$, or sulphionide of potassium. The same view was extended to the compounds of ammonia, which themselves might be regarded as of organic origin; and as some undoubted compound radicals like cyanogen were discovered, at length all organic chemistry came theoretically to be arranged on these analogies. Thus alcohol was originally supposed to be a compound of olefiant gas and water, $C_4H_4,2HO$, being its actual composition, while ether is $C_4H_4,HO$; but the HO in either is capable of being replaced by H,Cl or muriatic ether, $C_4H_4,HCl$. Now, on the analogy of the chlorine doctrine, to make this a chloride we must have $C_4H_5,Cl$, or a chloride of a new radical—ethyl; according to which view, it becomes easy to represent ether as $C_4H_5,O$, or oxide of ethyl, and alcohol as $C_4H_5O,+HO$, or hydrate of the oxide of ethyl; and so with numerous other groups.

In inorganic chemistry changes in the mutual action of the members of groups take place, according to the analogy or type of some leading member of the groups; as, for instance, in the class of halogenous elements, and their compounds according to the type of chlorine. The same is the case in organic chemistry: and in general one analogous body, according to the strength of its chemical relationship, may be substituted for another; but these relations are not always so well defined in organic chemistry; and, indeed, sometimes bodies are substituted for one another, in opposition to the rules of the electrochemical theory, as understood in inorganic chemistry. For instance, chlorine is often substituted for hydrogen; *i. e.*, an electro-negative for an electro-positive body; and iodine, bromine, &c., or oxygen, may be so substituted for hydrogen. In acetic acid, $C_4H_3O_3,HO$, the 3 eq. of hydrogen in the anhydrous acid, may be replaced by 3 eq. of chlorine, and the new compound, chloro-acetic acid, has properties similar to acetic acid. Many other examples might be cited. In other instances the substitution is strictly according to the electro-chemical law; as in the compounds of formyl, when for $C_2H$ formyl, in combination with oxygen in formic acid, or $C_2HO_3$, we have $C_2HCl_3$ for chloroform; $C_2HBr_3$ for bromoform; and $C_2HI_3$ for iodoform.

The properties of the bodies formed in this way by substituting one for another, in combination with a base, are generally similar; and there are not wanting instances of isomorphism, although these organic

substances are much more rarely found crystalline. Sometimes, different organic principles are substituted for one another in a curious manner; for several of the compound organic radicals can be substituted for each other, in combination with amidogen, formed by the displacement of one atom of hydrogen in the ammonia by one of the organic radicals; thus, instead of ammonia, $H_3N$, we have with methyl, $C_2H_3$, a substance called methylamine, $C_2H_5N$; with ethyl, another called ethylamine, $C_4H_7N$, and so on. This doctrine is of great practical value, as it can almost be foretold, a radical being once ascertained to be combined with a principle in a compound, what other radicals or principles may be substituted for either of these, and then what new compounds may be formed.

Organic compounds differ much from inorganic bodies, in their greater instability. Thus especially those which have been formed under the influence of life, and which cannot be produced artificially, on the withdrawal of the force which can create them generally undergo changes, especially when exposed to air and moisture, which are of the nature of slow combustion, fermentation, or putrefaction. These changes may be summed up under the heads of slow oxidation, or eremacausis; as, for instance, in the decay of wood, where the hydrogen and a portion of the carbon are slowly oxidated, and which is supposed to be analogous to the process of respiration, and to go on when nutrition is suspended. This process is so very analogous to fermentation, as that one body in a state of eremacausis brought into contact with another body not in that state, has a tendency to induce a similar change in it. But it does not absolutely require the presence of a ferment to induce it. In fermentation, complex bodies are divided into simple ones without any chemical action of the ordinary kind having been caused. But the presence of a third substance is necessary to commence the separation, although we are unable to perceive any way in which we can chemically effect the change. In short, what takes place is like the action of spongy platinum in causing the union of oxygen and hydrogen, except that separation and not union is the result. This action of the third substance or ferment is, therefore, classed with those catalytic phenomena already referred to. When yeast is put into contact with sugar, the result is the formation of carbonic acid and alcohol. In these bodies the elements are united in much stronger combination than previously in the sugar. The yeast, therefore, has brought about this change, to which, it may be supposed, there was already a tendency. Yeast is obtained from gluten, and put in contact with water, undergoes a further change; being in this state of change, it sets likewise the molecules of the sugar in motion; and if it meet with any gluten in the saccharine substance, would form fresh yeast. There are analogies to fermentation in some inorganic bodies; for instance, the action of peroxide of hydrogen on some metallic oxides, and the solution of an alloy of silver and platinum in nitric acid, when the solution of the silver determines that of the platinum, which of itself is insoluble in that acid.

Putrefaction is analogous to fermentation; it requires the presence

of air or water; when the change is once commenced it goes on, and leads to the formation of more stable compounds. An excellent example of it is shown in the putrefaction of the urine when the urea is resolved into carbonate of ammonia, and more stable compounds than the other animal principles which that fluid contains are formed.

The doctrine of fermentation has been supposed to be analogous to the propagation of diseases like small-pox, and the contagious principle, whatever it may be, likened with some plausibility to the ferment.

Fermentation and putrefaction differ principally in the formation of ammoniacal compounds; in the latter, from the abundance of nitrogen in certain substances, and the fetid nature of the bodies formed.

Organic substances, when heated in close vessels, are subject to what is called destructive distillation. Fatty bodies, wood and coal, and animal substances, yield respectively different kinds of products. The oxygen contained in the substances themselves is able to suffice for an imperfect combustion. The products are very various; the residue,—inorganic matters and carbon.

## ORGANIC ANALYSIS

Is of two kinds. First, the obtaining of the immediate principles of animals and vegetables, as they exist in them, and the separation of the various principles when mixed from each other out of the tissues, which may be termed *proximate analysis ;* and *ultimate analysis*, or the determination of the ultimate elements of the organic compounds, which are, for the most part, the four elements, —carbon, oxygen, hydrogen, and azote. The separation of the organic immediate principles from the tissues of animals and vegetables, and of the principles combined among themselves, as organic acids from organic bases, is conducted upon the same rules as inorganic analysis; but the determination of the carbon, oxygen, hydrogen, and azote, is conducted upon a plan to which the name of *organic analysis* is especially given. Of this process, to which modern chemistry owes so much, it is proposed to give a short description.

Ultimate organic analysis may be divided into two parts: first, the analysis of the amount of carbon, oxygen, and hydrogen which bodies contain; and, second, an additional analysis requisite for bodies which contain azote.

The first requisite in organic analysis is to have the substance employed quite dry. For this purpose it is placed in a bent tube, which is immersed in a water or other bath according to the temperature required. This tube communicates at one extremity with a tube containing chloride of calcium, and at the other with a tube which is connected with a receiver containing water, and having a stopcock at the bottom; so that, on turning the stopcock, the water running out draws a current of air through the whole apparatus. Thus the air dried by passing over chloride of calcium passes over the substance heated in the bath, and before it enters the apparatus from which the

water is running to fill the vacuum produced there, it passes through another tube which, being exposed to the air, shows any condensation of water that may take place. This process is continued until no water is thus condensed. If the amount of water in the substance so dried requires to be estimated, it is weighed in the tube before it is dried, and afterwards. Sometimes an exhausting syringe, with a chloride of calcium tube between it and the substance to be dried, is employed; the latter, in a tube, is placed in a hot bath of some kind, and air removed by the syringe, so that it is dried in vacuo, fresh air is allowed to enter by a stopcock, and pass through the chloride of calcium tube, and enter the apparatus containing the substance to be dried. This air is again removed by the syringe, and at last complete exsiccation is produced. A known weight of the substance dried being now obtained, it is mixed, in a mortar, with a suitable quantity of oxide of copper, in the tube called the combustion tube, in fig. 38,
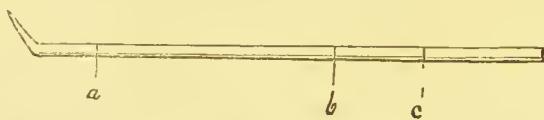


Fig. 38.

From the extremity to $a$ is the oxide of copper; from $a$ to $b$ the substance to be analysed and oxide; from $b$ to $c$ the rinsings of the mortar; and from $c$ to open extremity more oxide.

connected with the tube containing chloride of calcium, which itself is connected with an exhausting apparatus. The combustion tube is then placed in sand of the temp. of 120°; the air is then drawn by the exhausting syringe over the chloride of calcium, as long as any moisture can be observed in the tube, even when it is surrounded by cloth dipped in ether. In mixing the oxide of copper with the substance, the following precautions are to be attended to, it being understood that the oxide is either fresh prepared, or has been again ignited: 1st, the mortar must be smooth, unglazed, and must be hot; 2nd, it must be first rinsed with oxide of copper, which is not used for the operation; 3rd, the substance is to be gradually and equally mixed with the oxide. Before the mixture of the substance and the oxide are introduced, a quantity of pure oxide must first be introduced; then the mixed oxide and substance to be analysed. Then the mortar must be rinsed out with more oxide of copper, and this introduced; and, lastly, the tube must be filled up to the mouth with pure oxide of copper. These spaces occupied by their respective mixtures are shown in the figure. The whole of the contents of the tube being thus dried as described, two weighed tubes, one containing chloride of calcium, and the other solution of potass, as shown in the figure 39, are adjusted as described in the explanation of the diagram. Care is taken that the mixture in the combustion tube should be dis-

posed so as to allow some room for escape of air, or rather gases, when it is heated.
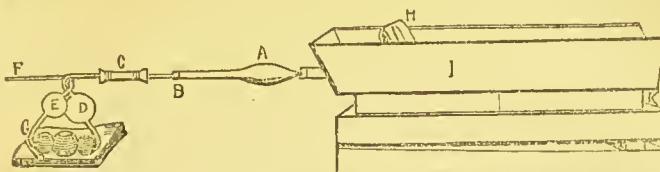


Fig. 39.

I furnace; H partition between the fuel and end of furnace ; A to B chloride of calcium apparatus; C caoutchouc connecting potash apparatus.

The combustion tube is then put into a furnace, like that represented in fig. 40. This furnace is a trough made of sheet iron, with
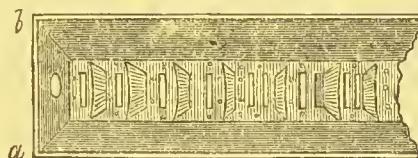


Fig. 40.

apparatus like slits at the bottom and diaphragms, on which the tube may rest, as shown in the figure. Its breadth and its depth are about three inches, and its length twenty-two or twenty-four inches. It is placed upon bricks as shown in fig. 39, and by means of a wedge towards the extremity K of this figure, it can be elevated at the open extremity. The mode in which the combustion-tube is supported in the furnace is shown in the sectional diagram 42. By means of the
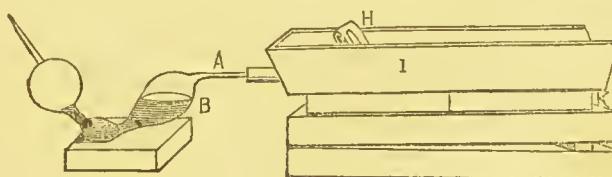


Fig. 41.

sheet-iron diaphragms (see H figs. 39, 41) a space is kept between the extremity of the furnace at which the combustion-tube passes out, and the body of the fire. The furnace being then filled up with red hot charcoal in a gradual manner, the slight inclination shown in fig. 39 being given, the combustion of the charcoal is then rapidly increased by fanning with a piece of pasteboard, and kept up as long as gas passes through the potash apparatus. As soon as the combustion is complete, the solution of potash mounts into the bulb of D, fig. 39, the nearest the apparatus, from the absence of more gas coming off; but the great size of this bulb prevents the fluid going into the apparatus. The charcoal around the combustion tube towards $a$,

fig. 38, is then removed, and the point nipped off, and a tube, as at B, fig. 42, placed over it. The orifice of the potash apparatus is then connected with a suction-tube (see I of the same apparatus), and all the carbonic acid and watery vapour that remained in the suction-tube are thus drawn through the apparatus. The experiment is now complete, and all that remains is to remove the chloride of calcium tube and potash apparatus, and weigh them as speedily as possible.

The object, then, of this analysis is to oxidate the carbon and hydrogen which organic substances contain, at the expense of the oxide of copper, which imparts oxygen to them, and the result is the formation of water and carbonic acid. The former is absorbed by the chloride of calcium; and, of course, from the calculation of its weight that of the hydrogen in the substance can be ascertained. In the same way, the carbonic acid is absorbed by the potassa; and from the increase of weight of the liquor potassæ, the amount of carbon in the carbonic acid absorbed can be estimated. In such a case as sugar, which is composed entirely of carbon, hydrogen, and oxygen, the subtraction of the quantities of the two former ascertained by the analysis gives the weight of the latter. A very large quantity of oxide of copper, in proportion to the amount of material, is required—as much as from 1,000 to 1,200 of the former to 6 or 7 of the latter.

When it is necessary to ascertain the quantity of nitrogen present, different modes of analysis are adopted; but the only one which it seems necessary to mention here is that styled the method of Will and Varrentrapp, which is perfectly adapted to the analysis of most organic substances, being, where it is applicable, highly accurate, while, at the same time, it is exceedingly simple. It depends upon the fact, that most azotised substances, when heated to a red heat in contact with potassa, evolve their azote in the form of ammonia. The water of the hydrate of potassa is decomposed, its oxygen goes to the carbon of the organic substance, while its hydrogen unites with the nitrogen, forming ammonia. In some compounds of nitric acid, and some of the inferior oxides of azote with organic substances, so much nitrogen is present, that the hydrogen evolved from the decomposition of the water of the hydrate of oxide of potassium is insufficient to convert it into ammonia; but the method of Will and Varrentrapp is applicable to the analysis of most azotised organic substances, and especially to those with which the medical man has to do. In practice, as hydrate of potassa alone would destroy the tubes in which the combustion is carried on, a mixture of this substance with caustic lime is used, in the proportion of three parts of the latter to one of the former, or two parts of caustic lime and one of caustic soda, which of course acts on the same principle as the hydrate of potassa. A combustion-tube is half filled with a mixture of the warm compound of potassa, or soda, and three to six grains of the substance to be analysed, mixed in a mortar, as in the analysis for hydrogen and carbon with oxide of copper. The mortar is then rinsed out with more of the mixture of lime and the alkali, and the tube filled up with this to about an inch from its mouth. A little ignited asbestos is then put in the mouth of the tube. It is then

connected by a cork with a bulbed apparatus, like that shown in fig. 41, containing muriatic acid. The combustion-tube is then heated in the furnace, as in the former analysis for carbon and hydrogen. When the combustion is commenced—which ought to be so managed as to begin at the anterior part of the tube—the screen, H, must be drawn back, until the combustion reaches that portion of the tube containing the organic substance. This will be known by the white fumes of muriate of ammonia which appear at B ; the combustion must then be conducted gently, as long as gas passes from A through the liquid at B. The combustion should be strongly urged towards the close of the operation, until the mass in the combustion-tube is not merely charred but white : the point of the combustion-tube is then to be broke, and air sucked through the apparatus, as in the analysis for carbon and hydrogen.
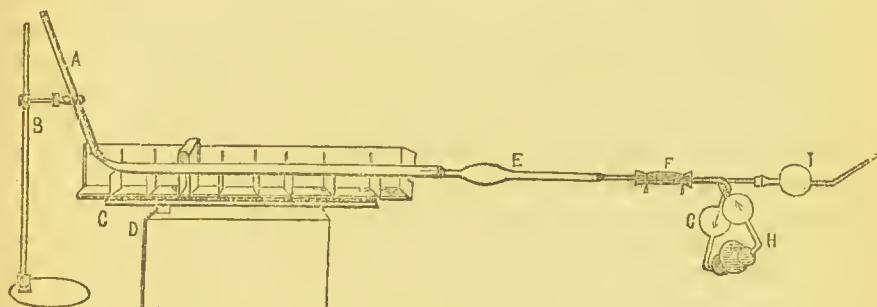


Fig. 42.

The object, then, has been attained, of obtaining all the ammonia disengaged from the substance in the form of muriate of ammonia in B ; for it is clear that any carbonate of ammonia disengaged would be reduced to that state. The apparatus is then removed, and its contents received into a vessel; it is then well washed, until the washings, in fact, show no trace of acid, and the washings added to the original contents. The whole is then mixed with excess of pure bichloride of platinum, and the whole evaporated to dryness in a porcelain dish, in a water bath. The residue is treated with a mixture of two parts of anhydrous alcohol, and one of ether. This dissolves out the excess of bichloride of platinum, and leaves the ammonio chloride of platinum. The residue is collected on a filter, dried, and weighed. As the formula for this substance is $NH_3HCl,PtCl_2$, and eq. 223, out of which only 14 are azote, the amount of the latter may be thus calculated. This calculation may be corrected by igniting slowly the filter and salt, and finally igniting strongly, so as to leave the platinum, the weight of which ought to correspond to the quantity of the salt, according to the proportion 98·68 to 223 parts. If the organic substance is difficult of combustion, chromate of lead is substituted for oxide of copper. This should always be done when the organic substance contains chlorine, as the chloride of copper is volatile, but not the chloride of lead. In the same way, the presence of sulphur in an organic substance requires

precautions. The sulphur is converted into sulphurous acid, and a tube containing the peroxide or puce oxide of lead is placed beyond the chloride of calcium tube to retain the acid gas.

It is clear that such an analysis only gives the proportions of the ingredients, without giving the chemical equivalent of the substance, or the mode in which the elements are combined. These are deduced from other considerations. Thus, if the organic substance be an acid, it is saturated by some inorganic base, and then displaced from this base by an inorganic acid. As the equivalent of the inorganic salt thus formed is known, it is clear that the quantity of the inorganic salt must bear the same relation to its equivalent which is known, as the quantity of the organic acid and its inorganic base does to its equivalent; and as that of the latter is known, it is easy from it to calculate that of the organic acid required to saturate it. This equivalent then being obtained, it is easy from this, having found the proportions of the elements of the organic acid by analysis, to apportion these according to the atomic system. In like manner, organic bases are saturated with inorganic acids, and then an inorganic base is substituted for the organic one, and the same mode of calculation applied. When the organic substance is neither base nor acid, the only mode of calculating the equivalent is by putting it in the simplest form its composition, as given by the analysis, will admit of. There are substances about whose equivalents and formulas there may of course be considerable doubts. Even when the calculation of the atomic weights of organic substances can be most controlled, there will still occasionally be the same difference of opinion that exists in inorganic chemistry as to the precise weight that should be fixed on.*

In those cases where the organic substance is neither base nor acid, some idea of its atomic weight may be derived from the compounds formed, where the substance is acted upon by other bodies.

In the case of volatile substances the determination of the specific gravity of the vapour furnishes a valuable control over that of their atoms, as we know that, with some exceptions, the atomic weights of gases are as their specific gravities.

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## CHAP. I.—ALIMENTARY SUBSTANCES.

The first group of organic substances which may be considered, are those of the character of aliments, which form one of the most interesting and important classes in every respect of organic substances.

* The reader will be prepared to understand how different writers sometimes prefer different formulas for organic substances. For example, the atomic weights of many of the albuminous group are made much greater now than formerly.

These may be divided into three groups :—first, the albuminous—whether animal or vegetable ; second, the hydrocarburetted constituents of animals and plants, such as sugar and starch ; and, lastly fatty bodies. Of these groups, the albuminous substances include all the four elements, carbon, oxygen, hydrogen, and azote ; the hydrocarburetted elements by their composition being represented by the addition of carbon to water ; the fatty bodies contain carbon to a very small quantity of oxygen.

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SECT I.—ALBUMINOUS BODIES AND SUBSTANCES DERIVED FROM THEM.

When these substances are heated much above the temperature of boiling water in close vessels, they begin to be decomposed ; and if distilled and calcined, they yield fœtid gases, and liquids and solids, which contain carbonate, prussiate, and hydrosulphate of ammonia, oily and watery fluids, and, in the end, a black, shining, and spongy coal, which further heated in the open air gives a saline residue. Heated in contact with air from the first, they burn with a well-known effluvium. These substances kept from water and air can be preserved ; but, removed from the living animals and vegetables in which they have been produced, and exposed more fully to air and moisture, they undergo the phenomena of putrefaction already referred to.

They were supposed at one time to be definite compounds of a substance called proteine,* but this view is now discarded. Proteine was supposed by Mulder, the author of the theory, to have the composition $C_{40}H_{31}N_5O_{12}$, and that the crystalline of the lens, caseine, vegetable gelatine, albumen of the egg, fibrine of the blood, and other principles formed only in disease, were combinations of sulphur, or phosphorus, or oxygen with proteine in definite proportions. Proteine was obtained, as it was supposed, when albumen, fibrine, or muscular tissue is dissolved in a solution of potash pretty concentrated, kept at a temperature of rather more than 120° ; this causes the formation of some sulphuret of potassium and phosphate of potass at the expense of the sulphur and phosphorus existing in the organic substance ; then, by the addition of slight excess of acetic acid, a gelatinous matter is thrown down, which is collected on a filter and washed as long as it yields traces of acetic acid, or rather of acetate of potass ; the result is proteine. It now began to be discovered that substances so complicated as those albuminous principles, could not be so easily reduced to mere compounds of proteine ; that the process did not always yield the same substance ; and that the result was not necessarily by any means free of

* This substance is generally, in all respects, like coagulated albumen, only it is dissolved more readily in alkaline and acid solutions. By some it was supposed to be an allotropic condition of albumen, which, in fact, seems the true view.

sulphur; and the theory of proteine may now be considered a matter of history, leaving only to scientific men a warning how they so readily accept captivating theories. These albuminous substances may be treated of under four heads :—

1st. Albumen properly so called; 2nd, fibrine; 3rd, caseine, gluten, albumine, &c.; 4th, the products of the artificial alteration of albuminous substances; 5th, the products of their vital alteration.

1. *Vegetable and Animal Albumen.*—This principle is found fixed in the solids, or circulating in the fluids of organised beings. The serum of the blood and white of egg form the purest specimens of albumen. It does not exist even pure there, being accompanied by some salts and oily matters. Pure animal albumen is best obtained by evaporating the serum of blood, or white of egg, at a temperature of little more than 120°. There will remain a solid transparent layer, like glue. This is powdered, and then treated with ether, and then with alcohol, to remove fatty matters. The salts, however, still remain; and if it is desired to remove them, the white of egg is first coagulated by muriatic acid, the coagulum dissolved by a gentle heat in the acid considerably diluted; and then albumen may be reprecipitated by carbonate of ammonia, washed with water, and then treated successively by ether, alcohol, and water.

Vegetable albumen is best obtained by taking potatoes, cutting them to pieces, and allowing them to digest in water containing 2 per cent. of sulphuric acid. This water is decanted after it has stood for 24 hours, and again it is replaced for the same time on fresh slices of potatoes. After several operations, a yellowish liquid is obtained, to which a little alkali is added, taking care to leave a slight excess of acid; the ammonio-magnesian phosphate contained in the potatoes remains thus dissolved; on being heated, the liquid allows flocculi of vegetable albumen to be precipitated.

Albumen then exists in two forms, soluble and insoluble, as is seen in comparing an unboiled with a boiled egg. The point of coagulation generally varies from about 140° to 160°. But it may, in some forms and in some animals, take place somewhat lower. Coagulated albumen can be re-dissolved in water under high pressure, but it has then lost the property of again coagulating. When albumen is long boiled in water, in which it has been coagulated, it changes in its nature, and becomes the substance which Mulder called tritoxide of protein.

Albumen forms numerous compounds with acids and salts, to some of which reference has been made.

The composition of albumen in 100 parts is C 53·32, H 7·29, N 15·7, S 13, O 22·39. Its formula is now represented $S_2N_{27}C_{216}H_{169}O_{68}$.

2. *Fibrine.*—It is not quite so certain that a substance perfectly identical with the fibrine of animals can be extracted from vegetables, as it is that albumen identically the same can be got from both. It is true that we can extract from the gluten or bird-lime of wheat a substance having many resem-

blances to fibrine, but it is not clear that they are identical. Vegetable fibrine is obtained from gluten by boiling with concentrated alcohol, and then with alcohol diluted. The greyish elastic fibrous residue is vegetable fibrine. According to some there is also a soluble gluten.

Animal fibrine exists in the muscular tissue, and in the blood; and in many of the other tissues. It is best obtained by stirring fresh drawn blood with a stick, and washing well what adheres to the stick, first with water, then with a little ether and alcohol, and then again with water. It still retains a quantity of salts, varying in the ashes from 1 to 2 per cent.

Fibrine thus obtained is a hard greyish mass; when still wet it retains 4-5ths of its weight of water. It loses this on being dried, and replaced in water reabsorbs three times its weight. It is not altered by a high temperature—say 280°. It is acted upon by heat like other albuminous substances, and putrefies like them in contact with air and moisture. It is acted upon by acids in a somewhat peculiar manner : like albumen, it is dissolved, but with some difficulty, by hydrochloric acid, and a violet or blue liquid formed; the solution is precipitated by the action of several agents, and by excess of water. Sulphuric acid causes fibrin to swell and become gelatinous. It is soluble in caustic alkalies, and is thrown down by acids and alkalies from their solutions. When fibrine is exposed to the action of water, and kept cool in close vessels for some time, a partial putrefaction takes place, and some of it is dissolved in the water, and possesses some of the properties of albumen. Fibrine from different sources differs a little in chemical composition and in some minor properties. The composition of fibrin of the blood in 100 parts, is C 53·9, H 6·99, N 15·58, S 1·50, O 21·83. Ash 0·28.* Formula $S_2N_{40}C_{298}H_{228}O_{92}$.

Musculine appears to bear the same relation to coagulated fibrine that albuminosine does to albumen. It has been ordinarily confounded with the ordinary fibrine. The principal difference between the two appears to be the superior solubility of the musculosine in dilute muriatic acid. It forms the base of muscular fibre, being united then with albumen, and with creatine and creatinine, excrementitious principles. Its composition is exactly that of the albumen of the blood.

3. *Caseine, Gluten, Legumine, &c.*—A substance exists in the milk which forms the essential part of cheese, and which is called caseine, and which closely resembles albumen. It is obtained by adding to fresh milk diluted sulphuric acid, and heating the mixture. A white clot is thus obtained, which is well washed, and dissolved in a concentrated solution of carbonate of soda, which gives a syrupy liquid; this solution, containing a slight excess of carbonate of soda, is left to itself in shallow vessels at a temperature of 68°, until the butter set free forms a separate layer at the top. The

* The quantity of ash in this analysis is much below the ordinary.

lower part of the liquid is removed by a syphon; it contains a combination of cascine and carbonate of soda. The caseine is thrown down afresh by sulphuric acid; and the precipitate treated with boiling water, when it partially dissolves. A little weak solution of carbonate of soda is then added, and the cascine thrown down almost pure. It is then washed with water, alcohol, and ether. Of course the intention of these processes is to free it from fatty bodies, salts, and acids with which it is mixed or combined.

Caseine is a white opaque body, very similar to coagulated albumen. It is inodorous, insipid, insoluble in water and alcohol. In the dry state it has a gummy aspect; its properties generally resemble those of the albuminoid group. Caseine itself reddens litmus, but does not give this property to water, in which it is slightly soluble. It forms neutral liquids with the alkaline carbonates, in whose solutions it is very soluble, and from which it is thrown down by all the acids except the carbonic. In sulphuric acid caseine swells up and gelatinises. Muriatic acid acts on it as on the other members of the albuminous group, forming the deep blue solution. The putrefaction of caseine gives rise to the formation of a great many compounds. Caseine is *not* coagulable by heat, and is thus distinguished from albumen. Its composition in 100 parts is C 53·6, H 7·1, N 15·8, O 22·6, S 0·9, and the formula, $S_2N_{36}C_{288}O_{90}$.

Gluten may be extracted from the flour of wheat, simply by well washing the latter on a cloth. The grains of starch are removed by the washing, and there remains a substance insoluble in water, gluey when moist, and yellow and translucid when dried. This substance consists of vegetable fibrine, caseine, and a substance called *glutine*. The former is obtained by treating the gluten first with boiling concentrated alcohol, and then with more dilute alcohol, when flakes are separated presenting a resemblance to animal fibrine, and which, at any rate, has the same ultimate composition. The alcohol on leaving these flakes and cooling, deposits, on cooling, a pultaceous caseous matter, analogous or similar to caseine; and still after cooling has in solution another substance named glutine. The latter closely resembles albumen, but is distinguished by its solubility in alcohol.

Of the remaining albuminous principles, one of the most remarkable is *albuminose*, or albuminosine. This substance has been confounded with caseine. Its non-coagulation by heat distinguishes it from albumen; and the fact that it is coagulated by acetic acid, but redissolved in excess of this acid, distinguishes it from caseine, which is not so redissolved. This substance is found in the chyme from the digestion of azotised substances, and exists in the blood in the proportion of from 4 to 6 per cent. It appears to be a preliminary form of albumen in some respects. After all the ordinary forms of albumen are withdrawn from the serum of the blood by its coagulation, the presence of this substance in the residue may be indicated by the test of acetic acid, and also because it is precipitated, like other substances of the kind, by salts of lead, mercury, and silver, and by alcohol; the precipitate in the last case being soluble in water. Its ultimate com-

position appears to be nearly the same as that of the other organic substances of the class.*

Legumine, an albuminous principle extracted from haricots and lentils, appears to have several points of analogy with albuminosine, and with *amandine*, a similar principle extractible from almonds. The same may be said of *vitelline*, a principle contained in the yolks of eggs.

Besides these albuminous principles, there are several modifications of albumen as the supposed essential digestive principles of the gastric and pancreatic juices; and the saliva and the vegetable principles known as *diastase* and *synaptase*, which are of the same class as albumen; the same may be said of ferment; but diastase is properly treated of under the head of starch, and ferments beside sugar. It may be doubted whether synaptase obtained from almonds differs from amandine. Globuline is another principle—a supposed modification of albumen, existing in the globules of the blood and of the crystalline lens. Its chief characteristic appears to be that when it is dissolved in water either alkaline or acidified, and the solution is neutralised, it has a great tendency to precipitate.

4. *Products of the Artificial Alterations of Albuminous Substances.*—The first of these to come under consideration would be such as are included in the proteine theory of Mulder as regular definite compounds. Of these such may be selected as appear to possess the most distinguishing characters.

*Leucine* exists in the pulmonary tissues and the liver; and is often formed during the decomposition of other tissues—and especially during the action of acids on these tissues. The best mode of obtaining it, is by treating the animal tissues, say ox flesh (or glue is used) with strong sulphuric acid, then, filtering, diluting with water and boiling for some hours, then saturating with lime, filtering and evaporating. The extract treated with boiling alcohol gives crystals of leucine. These crystals are of various shapes, plates or agglomerated needles, having a pearly aspect. Their appearance under the microscope is represented in fig. 43, they are soluble in water, soluble in boiling alcohol, and crystallise on the cooling of the liquids. They are volatile without decomposition. The formula is, $C_{12}H_{13}NO_4$.

According to Mulder, nitric acid forms with proteine an acid which he termed xanthoproteic, and with chlorine a chlorite of proteine. According to his formula the former substance differs from proteine, in containing 6 eqts. less of carbon and 5 less hydrogen, and 1 less azote; his formula for proteine being $C_{40}H_{31}N_5O_{12}$, that for xanthoproteic acid would be $C_{34}H_{24}N_4O_{12}+2HO$, while chlorine, when it coagulates albumen, forms a simple compound of a chlorous acid of the formula $ClO_3$ with the proteine. The action of nitric acid in

* It is found in large quantity in placental blood, and in the fluid of the allantoid, which would still go to show that it serves as a preliminary form of albumen.

colouring albumen yellow, forms a sort of test for this substance; the compound which is formed, on being dried, readily takes fire, and if heated pretty strongly to dryness, takes fire spontaneously, when the organic matter is burnt with a species of explosion.

Gluten and caseine in the moist state are altered, and give rise to several products, some connected with the fatty bodies mixed with the gluten, and especially with the caseine if not pure; and among these, two,—one termed by its first discoverer caseic oxide, now known to be leucine, or aposepedine, the other product he called caseic acid. These are produced as follows:—Moist gluten covered with water is left for some days to putrefy. When the disengagement of gases has ceased, the mass is diluted with water, filtered, and evaporated to the consistence of a syrup. The product of the evaporation being left in a cool place, a crystalline deposit is formed, having a disagreeable taste, and a smell like cheese. This product mixed with alcohol is in great part soluble, and a white substance is left—the caseic oxide, or aposepedine.

The portion dissolved by the alcohol includes the caseic acid, which is, in fact, the lactic acid.

5. *Products of the Physiological Alterations of the Albuminous Group.*—These are endless. Between the extreme alterations which take place in the various excretory principles, as urea, there are intermediate substances having greater resemblance to the ordinary principles of the group, undoubtedly distinct from them, but still connected with them by some strong analogies. For instance, the gelatinous substances: these are acted on by heat precisely as the albuminous substances, and have similar or analogous actions, with such reagents as the various metallic salts. They are known generally as gelatine. They are especially remarkable for the strong affinity with which they unite with tannine and alum, forming well-defined compounds, little alterable.

*Gelatine* can be extracted from the parings of the skin, the intestinal membranes, the tendons, and nearly all the soft parts of the animal tissues, on boiling them for a longer or shorter time with water. The glue of commerce prepared in this way constitutes an impure gelatine. In this first preparation, the gelatine is freed from soluble foreign matters, and obtained in the form of a jelly, which is collected on linen, and well washed with cold water. It is then dissolved in hot water, insoluble substances are deposited, the solution is filtered and precipitated by its own volume of alcohol, and the gelatine is thus precipitated. Gelatine may also be obtained either by removing the earthy matter of bones, or by submitting the bones to digestion in the vapour of steam, above the boiling point, in proper digesters. The gelatine is thus extracted in a liquid form, and allowed to cool in wooden moulds. The purest gelatine is obtained from the swimming bladder of the sturgeon, which forms isinglass.

Pure gelatine is a hard, dry, transparent, colourless substance, which is insipid and inodorous. It softens in cold water, but can only be dissolved with the aid of heat; hardly soluble in alcohol,

and not at all so in ether. The name of chondrine is given to a substance which is to be obtained by the decomposition of pure cartilage, by long continued boiling. It differs chiefly from gelatine, in being precipitated by acids, which the former is not. These principles are not to be regarded as pure immediate principles, entering into the composition of the body as such, like albumen and fibrine.

The following table shows, according to some analyses, the composition of some of these substances in equivalents.

| | S. | N. | C. | H. | O. |
|---|---|---|---|---|---|
| Albumen of the blood and muscles, proper substance of the muscles | 2eqts. | 27eqts. | 216eqts. | 169eqts. | 68eqts. |
| Albumen of eggs | 3 | 27 | 216 | 169 | 68 |
| Caseine | 2 | 36 | 288 | 228 | 90 |
| Fibrine of blood | 2 | 40 | 298 | 228 | 92 |
| Tissues affording gelatine | | 13 | 82 | 67 | 32 |
| ,, ,, chondrine | | 9 | 72 | 59 | 32 |

The variations in the analysis of these substances show that they have not the same precise composition in every seat; and therefore that they are not to be regarded as of that well-defined nature that is found amongst inorganic bodies.

When one part of glue is treated with two parts of concentrated sulphuric acid, and the whole allowed to rest for twenty-four hours, a clear and colourless liquid is formed. This is to be diluted with nine times as much water as it contains glue, allowed to boil for eight hours, replacing the water, saturating with chalk, filtered, and after being allowed to rest for some days, evaporated to a syrupy consistence. At the end of another period of days, a crystalline mass may be thus obtained, which was called sugar of gelatine, but is impure leucine.

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## SECT. II.—HYDROCARBURETTED ALIMENTS NOT FATTY.

The substances comprised in the second class of alimentary principles are starch, gums, mucilages, woody substances, and the different kinds of sugar.

These substances are of very simple composition; their constituents being carbon, oxygen, and hydrogen; and, moreover, the hydrogen and oxygen being present in the proportions in which they enter into water.

It is a most important point with regard to these bodies, that they do not, like those of the previous class, undergo changes in contact with air and moisture of the putrefactive or fermentative kind, unless some of the principles or substances of the albuminous class be present, when they, in most instances, rapidly undergo the changes included in the term fermentation. They undergo, under the influence of heat, changes very similar to those of the previous class, except such phenomena as cannot occur in the absence of nitrogen, sulphur,

&c.   The products of their distillation are acid, from the formation of acetic acid.   Acids, at least the stronger acids, char them ; sulphuric acid causes oxidation of a portion of their carbon and of a portion of their hydrogen, formation of sulphurous and carbonic acids.   Nitric acid in excess completely oxidates them ; but if its oxidising influence be stopped at a certain point, it causes the formation of acid compounds, such as oxalic and mucic acids.

These aliments have of late years had ascribed to them a too exclusive place in the nutrition of animals.   It was supposed that these were the exclusive combustible materials of nutrition, that they were concerned entirely in the maintenance of respiration and animal heat ; but recent observations show that in the body such substances can be formed from the albuminous principles of food.

The subject may be studied under the following heads : 1st, starch ; 2nd, ligneous principles ; 3rd, gums and mucilages ; 4th, sugars ; 5th, principles which result from the decomposition of the hydrocarburetted principles ; 6th, phenomena of fermentation.

1.  *Starch* (Fecula), $C_{12}H_{10}O_{10}$, or $C_{12}H_9O_9+HO$; sp. gr. 1·53.— Starch and fecula, although the same substance, chemically differ in their mode of preparation, the former being obtained from the cereals, where it is intimately united with gluten.   The first object is to get rid of the gluten : this being insoluble in water is rendered soluble by fermentation ; for this purpose, waters formerly used in the operation are employed.   After several days the gluten is reduced into soluble principles ; the starch, in great part insoluble, is retained at the bottom of vessels of water, and is well sifted and washed.   Or by repeated washings in a fine sieve, the grains of starch are carried through mechanically, while the gluten is agglomerated and remains.   The starch which has passed through is then treated as the whole farina was in the previous case, to separate any gluten which has passed the sieve.   By this means the greater part of the gluten remains.

Fecula, or starch, is prepared from potatoes, by, in the first place, crushing the potatoes in salt water ; and then throwing the grains on a sieve, when the grains of starch pass through.   It is then well washed, and dried at a moderate temperature.

Starch examined by the microscope is found to be composed of oval corpuscles, of generally from $\frac{1}{100}$th to $\frac{2}{100}$ths of an inch in diameter (see fig. 44).*   At one of the extremities, each has generally a kind of umbilicus.   Starch, in a state of extreme hydration, in moist air, may contain as many as 19 eqs. of HO.   In a dry atmosphere four.   Heated to 300° it is completely dried ; so dried, it soon recovers its water up to 4 eqs. in a moist atmosphere.   Heated to 400°, it is completely altered in its properties, becomes completely soluble, and is converted into dextrine.   Heated in water, the different layers begin to swell, the inner especially, and burst the outer. This begins at a few degrees

* They differ greatly in size in many plants, and are composed of concentric layers, which are harder externally than at the centre.

above 130°. With 15 parts of water, it forms the thick starchy solution. When digested with water in close vessels at a temperature considerably above the boiling point, it first forms a gum, like dextrine, and then some sugar. Starch is precipitated by alcohol, tannin, and some salts, and is dissolved by nitric and muriatic acids. Its principal peculiarity is its reaction with iodine. This has already been spoken of under iodine,—the colour disappears on heating. Numerous dilute acids dissolve starch and convert it into dextrine on boiling, and then into sugar. Diastase, an albuminous substance found in grains which have germinated, possesses the power, even in very small quantity, to effect this change. When starch is dissolved in strong nitric acid, it may be precipitated by means of water, a substance called xyloidine is precipitated, which is very explosive.

*Dextrine*, also called soluble starch, has the same formula as starch. It is best prepared by heating, in an air bath, starch in a very dilute solution of nitric acid, and then heating at a high temperature, and drying the solution.

*Diastase* seems intended to have the property of converting starch into sugar. One part of it will so convert one thousand parts of starch. Diastase is formed when the cereal grains and potatoes germinate. It may be extracted by macerating the grain (generally barley) germinated, and ground in water at from 78° to 85°, and squeezing it through a bag. It is then filtered, and heated to a sufficient point to coagulate albumen. The liquid is then filtered, and it is ready to act. If anhydrous alcohol is poured into it, the diastase is thrown down in flocculi. It may be dried at 115°. It is a white amorphous substance, soluble in water, insoluble in strong alcohol, which soon putrefies if moist, but if dry can be kept a long time. There are various forms in which starch is known, as arrow-root, cassava, tapioca, &c.

*Inuline*, obtained from the roots of different plants, has been represented as having a somewhat different composition from starch, but has nearly similar properties, except that iodine turns it brown, not blue.

*Lichenine*, prepared from Iceland moss, has the same formula, has greater power of gelatinising when boiled in water, and is turned green instead of blue by iodine.

2. *Lignine, or Cellulose*, $C_2H_{10}O_{10}$.—The *web* or cellular tissues of all vegetables appears to be formed of one principle, viz., the cellulose. When this structure is filled by the work of vegetation, with various products, it constitutes wood or other vegetable solids. This basic tissue lignine, however, filled with resinous, fatty, colouring or other principles, with acids, alkalies, or earths, is uniformly of the same physical and chemical characters. It is a white insipid substance, inodorous, insoluble in water, alcohol, and ether. Cotton and paper give a good idea of it. They are formed of it almost pure. Cold water has no effect on it; boiling water disintegrates it in those tissues where its formation is recent and cohesion feeble. It then resembles dextrine. Its sp. gr. is 1·5. The simultaneous action

of air and water alters it in time; carbonic acid is formed, and the result is the formation of humus. Distilled in close vessels it gives rise to empyreumatic products. Subjected to a lower degree of heat for some time it loses its character, and becomes analogous to the gums.

When rags are washed for some time with strong sulphuric acid, they disappear, and the acid becomes viscous. The mixture is then to be dissolved in water, saturated with chalk and precipitated by alcohol. Dextrine, is precipitated, and this, boiled with weak sulphuric acid, yields grape sugar.

If we take concentrated sulphuric acid and water in the proportion of 3 of the former and 1 of the latter, and pour it upon cotton in a mortar, and bruise the cotton then for half a minute, the liquor is converted into a substance which gives a blue colour with iodine. Caustic potass has a similar effect. When strong sulphuric acid is heated with lignine, it is decomposed, carbonic acid and sulphurous acid are disengaged, by distillation acetic and prussic acids are obtained, and a black carbonaceous mass remains. Common nitric acid converts lignine into oxalic acid when heated with it; concentrated nitric acid, left a moment in contact with it, forms xyloidine, which has some of the properties of gun-cotton.

Lignine, in a state of fine division, converted into a paste, and rolled under cylinders at a high pressure, forms paper. Hence an immense number of substances have been used for this purpose.

*Xyloidine*, $C_{12}H_9O_{10}NO_5$, may be prepared as described; a piece of paper put into nitric acid of sp. gr. 1·5, and allowed to remain for a very few minutes, then dipped in water and dried, forms a paper of extreme combustibility. *Gun-cotton, pyroxiline*, has a formula of $C_{12}H_7O_73NO_5$. The difference, therefore, between it and xyloidine appears to be, that in the former 1 atom of H is replaced by $NO_5$, and in the latter 3. Gun-cotton is prepared by steeping hot cotton in a mixture of 1 part of strong sulphuric and 3 of strong nitric acid for an hour, and then washing it well. A solution of it in ether forms collodion.

3. *Gums and Mucilages.*—These bodies are distinguished by the following characters:—1st, they form, with water, the thick and mucilaginous fluids, so well known. 2nd, while water swells or dissolves them, alcohol precipitates or contracts them. 3rd, treated with nitric acid, they give birth, in the first place, to oxalic acid, and further, to mucic acid, which is white and insoluble in water; thus distinguished from oxalic acid.

Gums present great differences in their action with regard to water. Some are soluble in cold water, to which they yield a principle called *arabine;* others, insoluble in cold water, swell only, but are dissolved by long continued boiling; this principle is called *cerasine;* others are merely greatly expanded by hot and cold water, but this expansion is to many hundred times their volume; their principle is called *bussorine.*

Solutions of gums become acid in the air; they are not affected by

tincture of iodine. Dilute sulphuric acid converts them by long continued boiling, first into a very soluble gum, and by prolonging the action into soluble grape sugar, and an insoluble residue like lignin.

*Arabin,* $C_{12}H_{11}O_{11}$, exudes from several species of acacia as a juice, which dries in the air. It is obtained principally from Senegal. Sp. gr. 1·4; has a brilliant conchoidal fracture. Its physical properties are well known. It contains about 16 per cent. of water, which it loses at 100°. It also contains some saline principles. It may be softened and drawn into threads at above 330°. A cold aqueous solution, containing more than 18 per cent., will not filter; nor when hot, if it contain more than 23. The distinctions between it and *cerasine,* which is the chief gummy constituent of the exudations from cherry trees and other similar plants, have been mentioned. *Bassorine* is obtained by exhausting gum bassora or tragacanth with cold water, when bassorine remains. It is distinguished by its property of swelling up with water, and becoming like a jelly. In ultimate composition these principles resemble arabine.

*Mucic acid,* saccholactic acid, $C_{12}H_8O_{14}2HO$. This acid is found in the products of the oxidation of gums, mucilages, or sugar of milk by nitric acid. One part of sugar of milk or gum is to be dissolved in six parts of $NO_5$ of sp. gr. 1·42, diluted with one part of water. The mixture is to be heated in a retort. The acid is gradually deposited on the cooling of the liquid. It is to be purified by repeated solutions in boiling water, of which it takes 10 parts to dissolve it. It is a white crystalline powder. It is insoluble in alcohol. Its salts are very insoluble. Boiled for a long time in water it becomes much more soluble. Subject to sublimation it loses carbonic acid and water, and a sublimate is formed not unlike benzoic acid. This acid, termed *pyromucic,* is soluble in alcohol, and very acid.

4. *Sugars.*—Formerly, many substances were ranked in this class from their taste alone, which are now well known to be of a different character.

At present, the bodies ranked as sugars have the following properties.—first, their chemical composition can be represented by carbon and water; secondly, they are soluble in water and alcohol; thirdly, under the influence of heat they are decomposed in giving birth to products which have the odour of *caramel;* fourthly, they are destroyed under the influence of ferments in certain determinate circumstances producing alcohol; fifthly, they are oxidised with extreme facility, and tend to form, when treated with nitric acid, oxalic and carbonic acids; sixthly, they are not precipitated by acetate or subacetate of lead.

Sugars may be divided into two classes. The first includes cane sugar, grape sugar, and the uncrystallisable sugar of fruit. Of these, there are many varieties. The second group includes sugar of milk and its modifications.

Cane Sugar, $C_{12}H_{11}O_{11}$, exists in many plants, especially the sugar

cane. Its characters are the following. It erystallises in large rhomboidal prisms. It requires a temperature of 356° to melt it; dissolved in a concentrated solution of eaustie potass, and a few drops of solution of sulphate of copper introduced, the liquor can be boiled without the formation of an abundant red deposit. Cane sugar can be boiled in contact with caustic potass without being sensibly eoloured. It is converted by boiling along with a little mineral or organic acid into grape sugar. Cane sugar does not ferment; but in eontact with ferments it is converted into fruit sugar, which is eapable of being fermented.

The ordinary masses of sugar are eomposed of agglomerated crystals, but when slowly crystallised, the form is as was stated, and the crystals are very beautiful; sp. gr. 1·6. This is the candied sugar. Sugar slightly moistened and melted, rolled upon marble tables, forms barley sugar. In this form it is vitreous and transparent. At the end of some time the barley sugar becomes opaque. A crystalline layer has formed at the surfaee which is easily detached. This is a change like that which crystals of iodide of mereury undergo when from yellow they become red.

At a temperature of 410° sugar is eonverted into caramel, and loses two equivalents of water.

*Caramel* is $C_{12}H_9O_9$. This is a black body, very soluble in water, whieh it colours brown. It is deliquescent, insipid, not fermentable, not soluble in alcohol; may be regarded as the basis of sugar. When the heat is further continued, acid products are obtained, inflammable gases, and a carbonaceous residue. Sngar is soluble in one-third of its weight of cold water, and in every proportion of boiling water, and little soluble in pure alcohol. A watery solution may be precipitated by absolute alcohol. By long-continued boiling in water, sugar is changed into grape sugar, and uncrystallisable sngar. A few drops of a powerful acid in water transform, on boiling, cane sugar into grape sugar. When sugar is acted on by the aid of heat with sulphuric aeid, formic aeid, and humic acid, and humus are formed. A saccharate of lime is formed, by dissolving at a moderate temperature hydrate of lime in a concentrated solution of sugar; the saccharate of lime may be precipitated by alcohol, and washed with boiling water. Its formula is $C_{12}H_9O_9,CaO,HO$. Sugar forms crystallisable compounds with the alkaline chlorides, and with several metallic oxides and salts. Several metallic salts boiled with sugar are either reduced to lower degrees of oxidation, or to the metallic form.

Sugar is prepared from the expressed juice of the sugar cane. This is heated to 140°, and slaked lime added, the mixture is then stirred and heated to near the boiling point. This serves to separate impurities and so eoagulate albumen. The fluid is more than once treated in this way. It is then filtered through animal charcoal, concentrated by boiling, and crystallised. The molasses are separated from the crystals, and the latter washed with a saturated solution of sugar.

Grape Sugar, or Glueose, $C_{12}H_{14}O_{14}$, exists in grapes, honey,

exists in the liver, according to recent researches. The characters of this species are the following. It crystallises with much more difficulty than cane sugar, and in a mammillated form. Heat softens it at 60°. Boiling in contact with alkalies colours it brown. Its boiling solution reduces instantly into red protoxide of copper the blue liquor formed by potass and salts of peroxide of copper.

Heat softens grape sugar at 140°, and melts it at 212°, and at that temperature it loses two equivalents of water, and is converted into uncrystallisable sugar. Its formula is then $C_{12}H_{12}O_{12}$. This is also the formula of fruit sugar. Grape sugar is less soluble in water than cane sugar. It is not so sweet. It is much more soluble in alcohol than grape sugar. It does not combine so easily with alkalies. With solutions of alkalies the liquid becomes brown, gives off a smell as of burnt sugar, and acid compounds are formed, which combine with the potass, and a brown matter is left. When acid solutions are boiled with grape sugar, formic acid is produced, and several brown or black compounds. Sulphuric acid concentrated without the aid of heat, forms a sulpho-saccharic acid.

Grape sugar may be extracted from grapes or raisins; the raisins are to be treated with alcohol, which removes the uncrystallisable sugar. They are then treated with water, which dissolves the grape sugar. The solution is then saturated with chalk, to remove some organic acids, decolorised and clarified by animal charcoal, evaporated, and crystallised. Nearly the same process is to be followed for honey.

When sugar is extracted from diabetic urine, the urine is first evaporated in a salt-water bath, then treated with strong alcohol. The alcoholic liquid is decolorised by carbon, then evaporated again to the consistence of a syrup; and then it is surrounded with a freezing mixture. In this way mammillary crystals are formed, which should be washed with strong concentrated alcohol until they lose all urinary odour. These should be allowed to dry on a filter and on blotting-paper. If these are re-dissolved in absolute alcohol boiling, the solution gives perfectly pure crystals.

Starch is immediately converted into grape sugar by adding to a mixture of 10 of sulphuric acid and 1,000 of water boiling, 400 parts of starch by small quantities at a time, saturating by chalk, concentrating, and decolorising. Gluten, albumen, and diastase, have the same effect as $SO_3$.

*Uncrystallisable Sugar, or Sugar of Fruit*, $C_{12}H_{12}O_{12}$. This sugar is characterised by its liquid state and its extreme solubility in alcohol. It ferments readily, and reduces the peroxide of copper as quickly as the grape sugar. It is formed in the beginning of the action of sulphuric acid on grape sugar, and is the product of its action on gum or starch. Alcohol takes it from honey, and abandons it on distillation.

Several kinds of sugar are susceptible of fermentation: modifications of these kinds described appear to exist; as, for instance, a sugar of ergot, and a kind found in a species of eucalyptus in New Holland.

An insipid sugar capable of fermentation exists in some kinds of diabetes.

*Sugar of Milk,* $C_{12}H_{12}O_{12}$, Is characterised especially by mucic acid being formed when it is treated by nitric acid, and it reduces the oxide of copper dissolved in caustic potass. It requires a temperature of above 99° and even up to 140°, to make it ferment. It is obtained by evaporating buttermilk to crystallisation. The product is re-dissolved, purified by vegetable charcoal, and re-crystallised several times. It forms regular hard solid crystals. These are soluble in $2\frac{1}{2}$ parts of hot and 6 of coldwater. It is insoluble in alcohol and ether.

Weak acids convert it into grape suar after a more or less prolonged ebullition.

By boiling with dilute acids it is converted into grape sugar.

Nitric acid converts it into oxalic and mucic acids. It requires more ferment than cane sugar to cause it to undergo alcoholic fermentation.

### 5. *On some Products of the Decomposition of the Hydrocarburetted Aliments.*

*Action of Nitric Acid.*—Besides the products already indicated, nitric acid gives birth, in oxidating the hydrocarburetted substances, to an acid which has received many names, as oxalhydric, oxysaccharic, saccharic.

The best mode of forming this substance is to treat one part of cane sugar with three parts of nitric acid of sp. gr. 1·025; the mixture is to be raised to a temperature not exceeding 112°. Potass is then added, and a barely soluble oxysaccharate of potass formed. In order to isolate oxysaccharic acid, an oxysaccharate of cadmium must be decomposed by sulphuretted hydrogen. This acid is very soluble in water and alcohol, hardly so in ether, and quite uncrystallisable.

*Glucic Acid,* $C_{12}H_8O_8 3HO$.—Grape sugar readily dissolves about one-fifth of its weight of lime in the form of milk of lime. After some weeks carbonic acid loses the power of separating the lime from the sugar, which is transformed into glucic acid; oxalic acid effects this separation; the insoluble oxalate of lime leaves the glucic acid at liberty. Glucic acid may also be obtained by precipitating the glucic acid formed by the prolonged contact of lime and sugar with subacetate of lead, and decomposing the glucate of lead by sulphuretted hydrogen.

Glucic acid is a white solid, of a gummy aspect, very soluble in water, and attracting water from the air. The salts formed by glucic acid are generally soluble; the alkaline salts acquire a brown colour when boiled in contact with air. The acid itself is also coloured when boiled in the air.

*Melassic Acid* is a brown matter, obtained by fusing the crystallised hydrate of barytes with grape sugar, and separating the barytes by an acid.

When saw-dust is treated with fused caustic potass, a substance is

formed analogous to humus, and it is found that acid compounds with the potass are formed.

*Ulmine*, $C_{40}H_{16}O_4$, and *Ulmic Acid*, $C_{40}H_{14}O_{12}$ are formed when sugar is treated by muriatic or sulphuric acids, at a temperature of 176°. Twenty-two parts of sugar, forty of water, and one part of concentrated sulphuric acid, are employed. The liquor acquires a brown colour, and deposits flocculi, the ulmate of ulmine. When this action takes place *in vacuo*, two similar substances, humine and humic acid, are supposed to be formed; both nitric acid and chlorine acting upon these substances form acid compounds.

*Crenic Acid*, $C_7H_8NO_6$, may be obtained by treating earth with hot water, and then exhausting it with a boiling solution of carbonate of soda. This alkaline salt dissolves the humic acid as well as the crenic and apocrenic acids. Humic acid is precipitated by sulphuric acid; the acid liquor is then to be filtered, it retains the crenic acid along with a modification of it, termed apocrenic. It is saturated at first with carbonate of soda, then acidulated slightly with acetic acid. It is then treated with acetate of copper, which precipitates the apocrenate of copper. The crenate remains in solution. It is precipitated by means of excess of carbonate of ammonia, and the crenic acid separated by a current of sulphuretted hydrogen. The crenic acid obtained from this solution is a yellow sour substance. Apocrenic acid hardly differs from the crenic.

The apocrenic acid closely resembles the crenic, and both the humic, which latter is similar to the brown substance produced by the action of $SO_3$ on sugar.

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## SUGAR IN THE ANIMAL ECONOMY.

Sugar exists normally in the parenchyma of the liver, in that portion of the vena cava below it, in the blood of the right side of the heart and the pulmonary arteries. There is hardly any sugar in fasting animals in the blood of the pulmonary veins, in that of the left side of the heart, in the aorta and its branches, or in the systemic veins. During digestion, more of it is found, where it exists, fasting, and a little of it where in the circulation it is not found in the fasting state. It is never found in the bile in the normal state. It is found from the 4th or 5th month of intra-uterine life. The urine of the foetus in the intra-uterine state contains glucose, and has all the characters of diabetic urine. In the latter period of intra-uterine life, it is sometimes wanting. In the disease called diabetes, it exists in several fluids where it ought not normally to exist, as the urine, saliva, &c. Cane sugar and fecula pass into the state of glucose in the animal economy. It is proved that glucose is formed in animals fed on a purely animal diet. This formation of sugar takes place in the liver. It is proved to be under the control of the nerves, is stopped by cutting the pneumagastric nerve, and increased during certain excitations of the nervous system, so that in experiments on animals,

on increasing the reflex action of the spinal cord by pricking it at the origin of the pneumagastric, the animals become diabetic. Sugar in the system when not in excess, is believed to pass into the state of the lactic acid.

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6. *Substances produced by the Fermentation of the Hydrocarburetted Aliments*:

The phenomena produced by fermentation are those of decomposition. Thus when sugar produces alcohol, the sugar is simply resolved into alcohol and carbonic acid. Thus $2(C_4H_5O+HO)+ 4CO_2=C_{12}H_{12}O_{12}$, the equivalent of sugar of fruit. Most instances of fermentation admit of an easy explanation, as far as the composition of the substances produced is concerned ; but if it is easy in this way to explain most instances of fermentation, it is by no means so easy often to explain what are the circumstances which give to fermentation a precise direction, and lead to the formation of particular substances rather than others. Thus lactic and butyric acids and alcohol may all be formed from sugar, and they occur in nearly similar mixtures, without it being possible always to say why one should be formed rather than another from the attending circumstances. For fermentation to take place, there must not merely be present the hydrocarburetted substance ; but another principle, *the ferment*, must also be there. This principle is of an albuminous nature. The secondary conditions in which the principles concerned are placed, determine the nature of the substances to be produced. If a quantity of sugar, dissolved in water, be mixed with yeast, in a tube over mercury, and the whole exposed to a temperature of from $77°$ to $86°$, the phenomena of fermentation may be observed ; the yeast will be carried to the top of the tube by the disengagement of bubbles of air ; and these bubbles will go on increasing, until at last the tube is filled with a gas, which on examination will be found to be carbonic acid. This process will go on as long as any sugar remains, and a very small quantity of yeast will be consumed. Cane sugar is first converted into grape sugar, or fruit sugar. Thus it is said to require six times as much yeast to make cane sugar ferment as well as grape sugar. The yeast which has been destroyed will be found converted into a grey substance without determinate form, insoluble in water, scarcely azotised, and quite inert. The azote originally in the yeast has been converted into ammonia. The solid matter of yeast may be obtained by diluting yeast with water, and filtering it, when the yeast is left upon the filter. I  is found, when examined by the microscope, to be composed of globules, which appear to be a species of fungus. Ferment dried is a hard, horny, demitransparent, greyish substance. When this is boiled with a dilute solution of potass, an azotised principle is dissolved, and one insoluble and non-azotised remains. The azotised matter has nearly the composition of albumen, which explains its putrefactive character. The non-azotised principle closely resembles cellulose or lignine.

Several salts, creosote, and other substances, possess the power of retarding or stopping fermentation.

Yeast possesses the power of acting upon albumiuous matters in contact with the saccharine, and converting them into yeast. Albuminous matters, in the absence of yeast, in the first place can produce fermentation; but they must first be converted into yeast, which requires the presence of air. Human brain has been found to have great power in producing fermentation.

It has been fancifully supposed that the corpuscles composing ferment, and which some have regarded as of an animal nature, might be considered as beings nourishing themselves with sugar and albumen, secreting carbonic acid and alcohol.

Lactic and butyric fermentations occur when sugar is fermented with cheese.

The compounds derived from the fermentation of sugar are—1st, alcohol; 2nd, ethers and alcoholic and ethereal combinations; 3rd, compounds resembling the alcoholic group; 4th, compounds of which bicarburetted hydrogen may be looked on as the base, aldehyde, &c.; 5th, acetic acid, &c.; 6th, compounds, of which acetoue may be considered a type, formed on the base of protocarburetted hydrogen; 7th, lactic and butyric acids; and 8th, mannite.

## I. Alcohol, $C_4H_5O + HO = C_4H_6O_2$.

Alcohol is obtained solely from sugar, by means of fermentation. In theory, it is supposed to be a compound of au imaginary radical, termed ethyl or ethyle, with oxygen and water. It is on that theory a compound of the oxide of ethyle with water. Ethyle is represented as $C_4H_5$, and ether is regarded as its oxide $C_4H_5O$; then alcohol is $C_4H_5O + HO$, or the hydrate of the oxide of ethyle. According to this view it consists of $\frac{1}{2}$ vol. ether vapour and $\frac{1}{2}$ vol. water vapour. In a volume the sp. gr. of the vapour would be $1 \cdot 2994 + 0 \cdot 3100 = 1 \cdot 6094$. But it cannot be formed from the union of these constituents; and perhaps its formula might be as correctly written, $C_4H_6O_2$, or $C_4H_4$, 2HO.

Pure alcohol cannot be obtained from the ordinary products of fermentation. These products contain from 6 or 7 per ceut., as in beer, to 50, or even 55 per cent. in spirits.* The mode generally employed is to take strong spirit of wine, and highly rectify it by distillation; and then agitate it with lime, or chloride of calcium, for some days; aud, finally, distil it from one of these substances. The sp. gr. of absolute alcohol is $0 \cdot 792$; it boils at $173°$. Ordinary spirit of wine contains 70 per cent. of alcohol, and has a sp. gr. of $0 \cdot 880$. Spirit of wine, rendered still stronger by redistillation, and hence termed rectified spirit, contains 90 per cent., and has a sp. gr. of $0 \cdot 825$.

Pure alcohol has not been frozen by the most intense artificial cold. Alcohol combines in all proportions with water. The union is accompanied with a phenomenon of contraction and heat. Alcohol

* Wines contain from 10 to 25 per cent. of alcohol.

produces a cold of —5° when mixed with snow. Alcohol vapour, along with oxygen, is highly explosive. If made to combine slowly with oxygen, through the intervention of platinum wire, as, for instance, by surrounding the wick of a spirit lamp with platinum wire, and after the lamp is lighted extinguishing it, a disagreeable and sharp odour is produced, which rises from the presence of aldehyde; which is formed from the loss of 2 eqs. of hydrogen by the alcohol. Chlorine, acting upon alcohol diluted with 10 or 12 parts of water, produces aldehyde and hydrochloric acid. Alcohol contains 20 per cent. of water, absorbs chlorine, and produces a mixture of several compounds, known formerly as heavy chloric ether. In absolute alcohol chlorine causes the removal of some of its hydrogen, and its replacement by chlorine, and forms the substance known as chloral, $C_4Cl_3O,HO$. Bromine has the same reaction. Iodine will remain long dissolved in alcohol without change, but probably has a tendency to the same action, and certainly something of the kind occurs in time. Alcohol dissolves a great number of inorganic compounds, as the hydrates of potass and soda; most salts very soluble in water, and a still greater number of organic compounds. Acids act on it, forming ethers.

## II. Ethers and Etherial Combinations.

ETHYLE, $C_4H_5E$, or Æ, supposed to be the basis of the ethers, is a gas formed by the action of iodide of ethyle and zinc. It is a colourless gas of sp. gr. 2·0, which is reduced to the liquid form at a pressure of $2\frac{1}{2}$ atmospheres. Several compound radicals are supposed to be formed by it. Like some others of the till lately imaginary radicals, when obtained, it is doubtful how far it is the radical of the group constituted after it theoretically.

ETHER, OXIDE OF ETHYLE, SULPHIC ETHER, $C_4H_5$. Ether is prepared by taking 3 parts of the sulphuric acid of commerce, and 2 parts of 85 per cent. alcohol; or, if a stronger alcohol be used, a smaller quantity of acid. If alcohol of 90 per cent. is used, 5 parts of it are mixed with 9 of sulphuric acid in a retort. The mixture is brought to boil; and, by means of a vent-tube passing through a cork in the tubule of the retort, a supply of alcohol is introduced as the distillation goes on, so as to keep the fluid in the retort at the original level. The condensing apparatus, already described for nitric acid, is to be used. It is said that, in this way, one part of sulphuric acid can etherise 50 parts of alcohol. Alcohol in small quantity, ether, and some water—very little of the last if strong alcohol be used—come over; and, if the process be carried too far, several acids and other products. In order to purify the ether, it is to be mixed with an equal volume of milk of lime, left in contact with it for some time, and then distilled from a hot-water bath.

The chalk removes the acid products that it may contain. The water is retained by the alcohol, and the first half of the product can be considered as nearly pure ether. If the ether be then digested in a retort with chloride of calcium, and distilled from this retort by being heated in a water bath, pure ether will be obtained in the receiver.

It is supposed that, in the first place, in this process a compound of sulphuric acid and alcohol is formed, in the proportion of two eqs. of sulphuric acid and one of alcohol, termed sulphovinic acid, and that the decomposition of this acid by heat is the cause of the formation of ether. This acid will contain $2SO_3 + C_4H_5O + 3HO$; and if we suppose the $SO_3$ to seize the water, the evolution of $C_4H_5O$ will be at once accounted for. Other explanations have been given, as that the agency of the sulphuric acid in separating the oxide of ethyle from its water is catalytic. It will be seen how, if the decomposition of the alcohol be pushed further, various acid compounds may be formed; in particular, sulphurous and carbonic acids and deposits of carbon appear.

Ether has a sp. gr. of 0·725 at 60. It boils at 76°. Its evaporation produces great cold. It is very combustible at an ordinary temperature. Exposed to the air it absorbs oxygen gradually, and forms some acetic acid, for $C_4H_5O + 4O = C_4H_3O_3HO, + HO$. Under the influence of a slow combustion like that which has been described of alcohol with the aid of platinum wire, compounds are formed like those produced in the case of alcohol, such as formic and acetic acid, acetal, and aldehyde.

Sulphur is soluble in ether in the proportion of one per cent.; phosphorus in a larger proportion in hot ether, and can be crystallised on the cooling of the liquor.

Chlorine has a remarkable action on ether, forming a series of compounds distinguished from the other compounds of chlorine with hydrogen and carbon, in containing oxygen as well. One of the compounds formed by the action of chlorine on ether contains no hydrogen. It has been termed perchloric ether. Its symbol is $C_4Cl_5O$. It is solid and crystalline.

Bromine is soluble in ether—and after a time exerts an action on it analogous to that of chlorine, and the liquid becomes colourless. Iodine is also soluble; but has less action.

Ten parts of water dissolve 1 of ether, and 36 parts of ether 1 of water. Alcohol and ether will mix in every proportion.

Heated in contact with the alkaline hydrates, ether produces acetic acid.

*Other Ethers.*—These are of two classes, and resemble the divisions between the haloid and other salts. Thus hydrochloric ether may be represented as $C_4H_5Cl$, or as $C_4H_5O,ClH$, while nitric ether is $C_4H_5O,NO_5$. Almost all the acids form compounds with the oxide of ethyle if we choose to regard it as such, but as they are similar, or, at least, analogous in their mode of formation and properties, it seems only necessary here to select two: viz., the hydrochloric and nitric as examples of the rest. The former may be taken as an example of the haloid salts of oxide of ethyle; and the latter of its compounds with the oxacids.

HYDROCHLORIC ETHER, CHLORIDE OF ETHYLE, $C_4H_5O,ClH$, or $C_4H_5Cl$, is formed when ether and strong muriatic acid are mixed together. A very good plan is to pass muriatic acid gas into alcohol until the latter is saturated. The liquid is then to be distilled, the gas disengaged is passed first through a washing bottle containing a little water, then through a chloride of calcium tube into a receiver

surrounded by a freezing mixture. It is a colourless liquid of a garlicky smell; sp. gr. 0·874; boils at 52°. Exposed to the sun's rays, it is decomposed, giving rise to a variety of compounds. The bromide and iodide of ethyle are analogous.

*Nitrate of Oxide of Ethyle,* $C_4H_5O,NO_5$, may be prepared by heating together a volume of pure nitric acid, sp. gr. 1·4, and 2 volumes of alcohol, sp. gr. 960 (about equal weights,) and about 15 grains of urea.* Alcohol and water come over at first, then nitric ether. On adding water to the product, the nitric ether separates; and at the close of the operation a heavy layer of nitric ether forms at the bottom of the receiver. The product is to be well washed with an alkaline solution, then with distilled water, then left for a day or two in contact with chloride of calcium, and distilled. The sp. gr. of this ether is 1·112, it boils at 185°, is insoluble in water, soluble in alcohol. It is a remarkably fragrant ether.

The compound of nitrogen, $NO_3$, also forms a compound with oxide of ethyle. Sulphuric acid does the same; and so, in fact, do all the acids; but as the processes and principles of their formation and their properties are analogous to those described, they are omitted here.

COMBINATIONS OF ALCOHOL WITH ACIDS AND SALTS.—Alcohol combines with a great many salts, chiefly chlorides, and forms definite chemical compounds. Thus dry chloride of calcium combines with it, and much heat is disengaged. If the alcohol is saturated, the liquor on cooling leaves lamellated rectangular deliquescent crystals, whose formula is $CaCl,2(C_4H_5O,HO)$.

Several of the ethers, especially the hydrochloric, have similar properties.

Alcohol combines with several acids, and forms acid compounds, which have the power of combining with bases.

*Sulphovinic Acid,* $2SO_3,C_4H_5O,HO$, is best prepared by mixing anhydrous alcohol and strong sulphuric acid in as nearly as possible the proportion of 2 equivalents of the latter, and one of the former. The acid liquid after some time is diluted with water, then saturated with carbonate of baryta, when a soluble sulphovinate and an insoluble sulphate of baryta are produced. The soluble salt of baryta is then treated with sulphuric acid, when sulphate of baryta is precipitated, and sulphovinic acid left in solution. It is incapable of being concentrated. It forms sulphovinates, which are obtained by precipitating the insoluble sulphovinates of baryta, lime, or lead, all prepared in a manner analogous to the sulphovinate of baryta, by carbonates or sulphates of the bases with which it is wished to form sulphovinates. These salts are almost always very soluble, crystallisable, and almost always hydrated, often having a very strong affinity for water. When distilled with other salts, they have a great tendency to etherify the acids of these latter. Thus, with acetate and formiate of potass, they yield acetic and formic ethers.

* The use of the urea is to destroy any peroxide of azote or nitrous acid which might be formed.

Similar *vinic* salts can be formed by the action of other acids on alcohol.

*Xanthic Acid*, $2CS_2, C_4H_5O, HO$, is prepared by adding the bisulphuret of carbon to a solution of caustic potass in alcohol, till it is neutral, and then by treating the mixture with muriatic and sulphuric acid. In a short time a milky liquor in formed, to which 4 or 5 volumes of water are added gradually. The xanthic acid collects at the bottom of the vessel in the form of an oil, which is to be washed with 50 or 60 volumes of water. It is a colourless oily liquid, with a powerful odour, acrid, sour, and bitter taste. It is insoluble in water, inflammable, and by heat is resolved into sulphuret of carbon and water. It forms alkaline and metallic salts, the former soluble, the latter insoluble. When the xanthate of lead is submitted to distillation it furnishes two principles, *xanthile* and *xantharine*.

### III. MERCAPTAN, $C_4H_5S$, HS.

is alcohol, in which the oxygen is replaced by sulphur, and the water by a sulphuretted hydrogen (hydrosulphuric acid). It is therefore a beautiful illustration of the doctrine of substitution. It is obtained by distilling from a water bath a concentrated solution of the sulphovinate of lime, of sp. gr. 1·28, mixed with an equal volume of a solution of potass of the same density which has been saturated with sulphuretted hydrogen. The product should be distilled over oxide of mercury and chloride of calcium.

Mercaptan is a colourless and transparent liquid, of sp. gr. 0·842, boils at 98°. It possesses a very disagreeable smell; is very inflammable; and burns with a blue flame. It dissolves sulphur and phosphorus.

Various compounds, analogous to mercaptan, are obtained by the reaction of various bases with mercaptan, in which the hydrosulphuric acid of the mercaptan is replaced by the sulphuret of a base. Of these the compound of the sulphuret of potassium with the sulphuret of ethyl, $C_4H_5S$, KS, is an example. The analogous compounds of lead and mercury are especially remarkable.

### IV. SERIES HAVING OLEFIANT GAS FOR THEIR TYPE.

In this group the alcohol is to be regarded as completely decomposed, the $C_4H_4$ separated from the 2HO, and the series of compounds constructed from the type of $C_4H_4$.

The olefiant gas has been already treated of; it derives its name from the circumstance of its forming an oily-like compound when it comes in contact with chlorine gas; and as this was first discovered in Holland, it is termed the Dutch liquid. It is a compound of one eq. of olefiant gas and two of chlorine, $C_4H_4Cl_2$; but the elements may be arranged as $C_4H_3Cl, ClH$, or hydrochlorate of a new imaginary radical *acetyle*. In this case the Dutch liquid would be the analogue of alcohol in a new series of compounds of *acetyle*, where chlorine takes the place of alcohol. Accordingly, we should have $C_4H_3Cl$, the analogue of

ether in the ethyle series; but there are other compounds derived from the action of chlorine on alcohol or ether, which cannot so well be placed under the imaginary series of compounds of acetyle, but must be considered as rather derived directly from olefiant gas, which it is true may itself be regarded as the hydruret of acetyle. Thus we have—

$C_4H_4$, olefiant gas—or $C_4H_3H$,

$C_4H_3Cl$, protochloride of acetyle,

$C_4H_2Cl_2$. Here we have a clear substitution of $Cl_2$ for $H_2$ in olefiant gas; but we get into another series, that of the radical formyle $C_2H$, halving the $C_4H_2,2Cl$, we get $C_2HCl$, or protochloride of formyle.

$C_4Cl_4$, protochloride of carbon or chlorethose,

$C_4Cl_3O$, chloroxethose.

———

$C_4H_4O_2$, aldehyde,

$C_4HCl_3,O_2$, chloral.

— —

$C_4H_4Cl_2$, Dutch liquid,

$C_4H_3Cl,Cl_2$, perchloride of acetyle.

———

$C_4Cl_4Cl_2$, sesquichloride of carbon,

$C_4Cl_4O_2$, perchloride of aldehyde,

$C_4Cl_3OCl_2$, chloride of chloroxethose,

$C_4Cl_4Br_2$, bromide of chlorethose,

$C_4Cl_3OBr_2$, bromide of chloroxethose.

This extensive group forms compounds with very many bodies; only the more important of the compounds themselves can be treated of here.

CHLORIDE OF OLEFIANT GAS (*Dutch liquid, hydrochlorate of the chloride of acetyle*), $C_4H_3Cl + ClH$. Dry chlorine has no action on olefiant gas, but if humidity intervene, an oily, colourless, heavy liquid of a pleasant odour and very sweet taste is formed. The best way of forming the substance is to cause the gases to unite in a Woulfe's bottle, having water at the bottom, and with a tube from it passing into another receiver under water. The liquor condenses in both receivers. It has a sp. gr. of 1·24, and boils at 185°. It readily burns, and gives out numerous vapours of hydrochloric acid. It is insoluble in water, but soluble in alcohol and ether.* From the further action of chlorine

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* This substance, and indeed almost all the class of ethers, and compounds of hydrogen and carbon, is a powerful anæsthetic agent. There is no reason to suppose it inferior in any respect to chloroform, and it would probably be safer. The only objection to its use would seem to be the expense of its present mode of preparation.

on olefiant gas results, first, $C_4H_2Cl_2,HCl$. This is obtained by preparing first the compound $C_4H_3Cl$, which is done by acting upon the Dutch liquid by an alcoholic solution of caustic potass, then a gas of the above formula, having an alliaceous smell, liquefiable at 15°, is disengaged. When this gas is passed into chloride of antimony, and the result distilled, there is formed a compound of the above formula, $C_4H_2Cl_2,ClH$. It is an oily ethereal body, which boils at 239°, and of sp. gr. 1·412. When this is decomposed by alcoholic solution of potass, it yields $C_4H_2Cl_2$, a volatile liquid of an alliaceous odour, which boils at 95°* Acted upon by chlorine, it yields $C_4HCl_3HCl$. This is an oily ethereal liquid of sp. gr. 1·576, boils at 275°; decomposed by potass it yields $C_4HCl_3$, and the final result of the action of chlorine on olefiant gas is the solid sesquichloride of carbon of Faraday, $C_4Cl_6$. This chloride, on being passed through a red hot tube, is decomposed into chlorine and protochloride of carbon $C_4Cl_6 = C_4Cl_4 + Cl_2$.

The action of bromine or iodine, especially of the former, on olefiant gas, is analogous to that of chlorine.

Anhydrous sulphuric acid absorbs olefiant gas, and forms a white crystalline solid, a direct compound of the two, about whose exact equivalent proportions there is some difference of opinion. $2SO_3,C_4H_4$ is that adopted here. When thrown into water it is decomposed, *ethionic* and hyposulphuric acids being formed, for $2SO_3+C_4H_4+HO=C_4H_5O_2+S_2O_5$; but this acid is now understood to be a mixture of hyposulphate of ethyle, and another acid, termed carbylosulphuric.

The body termed *heavy oil of wine* is formed during the process for preparing ether, appearing towards the close of the process, when the etherification ceases. It is also formed during the distillation of a sulphovinate. As it is formed during very different circumstances, in all probability the substance known by that name is not always identical. It is an oily aromatic substance, heavier than water, boiling at 536°. It is a kind of sulphovinic acid, in which the basic equivalent of water is replaced by $C_4H_4$, eq. $2SO_3,C_4H_5O,C_4H_4$. In boiling water this body is decomposed into sulphovinic acid, and an oily compound, lighter than water, which has been termed *light oil of wine*. Light oil of wine should be regarded as a mixture; submitted, in fact, to the action of a low temperature, it yields a solid compound called *etherine*, and a liquid portion which floats above, termed *etherole*. Etherine, called also camphor of oil of wine, crystallises in white prisms, has a sp. gr. of 0·980, boils at 500°. Both it and etherole are isomeric with olefiant gas, $C_4H_4$. Etherine is soluble in alcohol and ether. It is tasteless. Etherole is best obtained by distilling equal parts of sulphovinate of lime and caustic lime. The result is a mixture of alcohol and etherole. The former may be removed by evaporation in vacuo over sulphuric acid. Etherole is a yellow liquid like olive oil, with a sp. gr. of 917, boiling at 534°. A similar fluid is obtained by distilling crude ether from caustic lime.

* Protochloride of formyl.

*Action of Bichloride of Platinum on Alcohol.*—Olefiant gas and chloride of platinum combine and form the following curious series with chloride of potassium and ammonia :—

$$C_4H_4PtCl + PtCl$$
$$C_4H_4PtCl + PtCl, KCl$$
$$C_4H_4PtCl + PtCl, NH_3$$
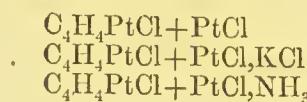
The first of this series is prepared by dissolving pure bichloride of platinum in alcohol. Several bodies are formed, as protochloride of platinum, aldehyde, acetic and hydrochloric ethers; that is to say, the bichloride is partly reduced, and the alcohol partly oxidated. The new product is in the solution, which is to be evaporated in vacuo over caustic lime. The residue is dissolved in water, acidulated with hydrochloric acid, and evaporated afresh. It forms a yellow gummy mass, which soon decomposes when kept, blackening when exposed to light. It is soluble in alcohol and water. The second of the series is obtained by distilling an alcoholic solution of double chloride of sodium and platinum, and saturating the acid residue of the distillation by carbonate of potass. At the end of twelve hours fine yellow crystals are deposited, which can be dissolved and crystallised.

ALDEHYDE, $C_4H_3O, HO$, or $C_4H_4O_2$). Hydrate of the oxide of acetyle.
Aldehyde is prepared by distilling, at a moderate heat, a mixture of six parts of sulphuric acid, four parts of water, four parts of alcohol of 80 per cent., and six parts of peroxide of manganese in fine powder. The retort should be large enough to hold three times the mixture. The receiver is to be surrounded with a freezing mixture. When the boiling in the retort is over, the liquid in the receiver is to be removed, and twice distilled from chloride of calcium. The product still contains water, alcohol, and formic and acetic ethers. Ether is then added to it, and it is saturated with ammonia ; crystals separate, which are to be well washed with ether and then allowed to dry. These crystals are a compound of aldehyde and ammonia. They are to be distilled from sulphuric acid in a water bath, in order to separate the ammonia. For this purpose two parts of the crystals dissolved in water are to be mixed in a retort with three parts of sulphuric acid, diluted with four parts of water. The receiver for the aldehyde is again to be surrounded with a freezing mixture. The aldehyde is then to be distilled from chloride of calcium, at a temperature under or not exceeding 85°. Aldehyde may be prepared by other processes ; it is formed when ether or alcohol is passed through a red-hot tube.

Aldehyde is a clear, colourless liquid, and possessed of a very strong odour ; sp. gr. 0·79 ; boils at 70°. It mixes with water in all proportions, also with alcohol and ether. It burns with a white flame. It dissolves sulphur and iodine. Chlorine and bromine act on it, and form chloral and bromal. Under the influence of air and light, it is soon resolved into acetic acid. It has the power of reducing oxide of silver thrown down from the nitrate. For this purpose it should be heated with nitrate of silver, and a solution of baryta, containing

the barytes in equivalent proportion to the oxide of silver. The vessel in which the operation is performed will be coated with silver like a mirror, and acetate of barytes remain in solution. Although aldehyde appears to have feeble acid powers, it does not affect the vegetable colours; and the crystalline compound which it forms with ammonia appears to be something of a salt.

There are two modifications of aldehyde of the same formula; *elaldehyde* is formed when aldehyde is long kept at the temperature of 32°. It is a crystalline mass, fusible at 34°, boils at 201·5. Metaldehyde is produced when aldehyde is long kept at the ordinary temperature. It is in the form of white prismatic needles, volatile at 201·5, without fusion.

*Aldehydic acid, Acetylous acid (Lampic acid)*, exists in combination with oxide of silver, when aldehyde is heated with excess of that oxide in water. It differs from aldehyde in containing one more eq. of oxygen. It is formed also, as has been stated, in the combustion of alcohol, in the wick of a spirit lamp, by means of a coil of platinum wire.

ACETAL, $C_8H_9O_3$. When alcohol is exposed to the influence of platinum black, in the presence of oxygen, a substance distinct from lampic acid is formed. To obtain it alcohol is put into the bottom of a jar, and in this several watch glasses are suspended, containing platinum black, moistened from time to time with water. The vessel is left for some weeks in a warm place. The alcohol becomes acid; acetal, acetic acid, acetic ether, and aldehyde are formed. The liquid is neutralised by carbonate of lime, and distilled; the product is left in contact with chloride of calcium as long as it is moistened. Thus the water and alcohol are separated. The remainder is distilled, and as the acetic ether and aldehyde are very volatile, they are separated first, the acetal only boiling at 203°. Acetal is a colourless ethereal substance, possessed of a peculiar smell; it is soluble in 6 or 7 parts of water, and mixes with alcohol in all proportions—sp. gr. 0·823. By the action of potash on acetal and aldehyde a brown resinoid matter is formed.

CHLORAL, $C_4HCl_3O_3$, may be regarded as aldehyde, in which three eqs. of chlorine replace three of hydrogen. Chloral may be obtained by the action of chlorine on aldehyde, but it is best prepared by passing a current of dry chlorine through absolute alcohol. The action is to be continued as long as hydrochloric acid is disengaged. The alcohol is at length converted into an oleaginous, sometimes crystalline, mass; this is to be digested with 3 or 4 times its volume of $SO_3$, to be agitated at a moderate temperature, when the chloral floats on the top of the sulphuric acid, as a limpid oil. This is decanted, and boiled for a short time to drive off muriatic acid and alcohol, and distilled from an equal volume of sulphuric acid, and finally distilled from freshly calcined lime.

Chloral is an oleaginous colourless liquid with a most penetrating and disagreeable smell, sp. gr. 1·5; boils at 202°. It is soluble

in alcohol and ether, and dissolves sulphur, phosphorus, and iodine. It forms a crystalline hydrate with one eq. of water, soluble in water, and which, boiled with caustic alkali, gives rise to the formation of an alkaline formiate and chloroform. $KO + C_4HCl_3O_2,HO = C_2HO_3,KO$ (Formiate of Potass) $+ C_2H,Cl_3$ Chloroform.

Chloral kept for a long time, like aldehyde, undergoes a metamorphosis, and a solid chloral is formed. Bromine has an analogous action on alcohol to that of chlorine, and a compound bromal is formed. Of the other compounds of chlorine and hydrurets of carbon of this series, *perchloride of aldehyde*, $C_4Cl_4O_2$, is chloral, whose last eq. of hydrogen is replaced by chlorine; and *chloroxethose*, $C_4Cl_3,O$, is prepared when the perchloride of ether is treated by sulphuret of potassium.

## V. ACETIC ACID, $C_4H_3O_3,HO$.

Acetic acid is ordinarily the product of the oxidation of alcohol, but it is also largely obtained from the distillation of wood. It also exists in the form of acetates in several vegetables. It also exists in the sweat, and probably in other cases, in the animal secretions.

The conversion of alcohol into acetic acid is illustrated by the action of spongy platinum on the vapour of absolute alcohol, or on alcoholic fluids, where the sole condition required is shown to be the oxidation of the alcohol. The spongy platinum may be replaced by various spongy bodies; and if alcohol is allowed to trickle over these, and the temperature be kept at about $77°$, and a sufficient quantity of air supplied, after a time the alcohol will be almost entirely converted into acetic acid. In the ordinary way of making vinegar, the alcoholic liquid should contain a ninth part of alcohol; to this some ferment must be added.

In the ordinary way of making vinegar, beech-wood shavings are placed in casks, whose sides are pierced with holes, so that the air may circulate freely. Into this cask the alcoholic liquid is allowed to flow. The shavings are first covered with vinegar, and a little vinegar mixed with the alcohol, so as to furnish the fermentative principle termed mother of vinegar. The vinegar which is formed escapes through holes in the lower part of the cask. If the process is not sufficiently complete in one operation, it is repeated in a second.

The change that takes place is obvious $C_4H_6O_2$ (alcohol) $+ 4O = C_4H_3O_3 + 3HO$. The first part of the conversion of alcohol into acetic acid must consist in the change of ethyle $C_4H_5$ into acetyle $C_4H_3$, by the oxidation of the two elements of hydrogen of excess in the former. The process may be regarded as one of eremacausis, or slow combustion; but eremacausis, as well as fermentation or putrefaction, is excited by the contact of a body in that state; hence the use of old vinegar in inducing the change. Old vinegar appears to contain a species of vinegar-plant analogous to what exists in yeast.

Vinegar may be made directly from sugar or starch, the stage of alcohol being, however, passed through in the process. For this purpose yeast and sugar are added to these substances, and they are left for a long time exposed to the air.

In the products of the distillation of wood are found a black tarry substance at the bottom, and above, a watery and acid portion. The latter is decanted and distilled. There are various methods of obtaining acetic or pyroligneous acid, as it is termed from its source, from the result of this distillation. One method consists in saturating it with chalk. The result is the acetate of lime, which is decomposed by sulphate of soda, acetate of soda and sulphate of lime being formed. This acetate is separated, evaporated to dryness, and slightly calcined, to decompose some organic matters. It is then distilled with sulphuric acid and rectified from dry acetate of soda.

Pure hydrate of acetic acid is obtained by distilling dry acetate of soda with concentrated oil of vitriol, in the proportion of three of the former and 9·7 of the latter. The product is then cooled to 23°, when crystals of the hydrate are formed. These are allowed to drain, and again exposed to cold; a pure hydrate is the result. This hydrate fuses at 63°, boils at 248°. When liquid it has a sp. gr. of 1·063. Its taste is pungent; and it blisters the skin, like the mineral acids.

When the vapours of acetic acid are passed through a porcelain tube, they are decomposed with production of carbonic acid, acetone, and some combustible gases.

Acetic acid is soluble in every quantity of water. Chlorine acts upon it, removing its hydrogen, and forming $C_4Cl_3O_3,HO$. Sulphuric acid also unites with it.

One hundred parts of good vinegar should saturate 8 parts of chalk.

*Sulphacetic Acid*, $C_4H_4O_4,2SO_3,3HO$, is prepared, first, by the reaction, aided by heat, of anhydrous sulphuric acid on hydrated acetic acid. The result is treated with baryta, and the barytic salt decomposed by sulphuric acid. Then the sulphacetic acid is decomposed by sulphuretted hydrogen, and the acid in solution concentrated, and crystallised with the aid of cold.

### ACETATES

Are generally soluble salts. They are all decomposed by heat, yielding acetone ; and by sulphuric acid yielding with the aid of heat a volatile product which can be collected, and which can be recognised as acetic acid by its odour, and its property of dissolving oxide of lead until the solution becomes alkaline. Carbonic acid then will precipitate two-thirds of the oxide dissolved as carbonate of lead. The acetates, treated with potass and arsenious acid, disengage a strong garlicky odour. Acetic acid is remarkable for the number of equivalents of some bases with which it forms compounds. Thus there are no less than six acetates of lead, from the neutral acetate $C_4H_3O_3PbO$, 3HO to the sexbasic acetate $C_4H_3O_3,6PbO$ : with copper there are also six, of which the neutral acetate contains $C_4H_3O_3,3HO$, verdigris, $C_4H_3O_3,2CuO,6HO$, while the polybasic acetate is said to contain 48 equivalents of copper and 24 of water to one of acetic acid.

*Chloracetic Acid*, $C_4Cl_3O_3HO$.—It is obtained by exposing the monohydrate of acetic acid to the action of dry chlorine under the

influence of light. It crystallises in rhomboidal needles. These have a slight peculiar smell, and a sharp caustic taste; sp. gr. 1·617, melts at 113°, boils at 293°. When heated in the presence of an acid it is changed into an alkaline carbonate and chloroform. It forms soluble salts with bases.

## VI. COMPOUNDS WHICH MAY BE REGARDED AS HAVING PROTOCARBURET OF HYDROGEN, $C_2H_4$, AS THEIR TYPE.

A series of compounds are related to the type acetic acid, of which the principal are chloroform, and its analogous bodies, acetone, and the series of cacodyle.

Acetic acid, exposed to the catalytic action of spongy platinum at a temperature a little above the boiling point of mercury, is resolved into carbonic acid and light carburetted hydrogen; for $C_4H_3O_3,HO = 2CO_2 + C_2H_4$. When chlorine acts powerfully upon protocarburet of hydrogen, it forms chloroform and perchloride of carbon. In both these cases the hydrogen is removed by the chlorine, and replaced by it in equivalent proportions. Thus $C_2H_4$ corresponds to $C_2H,Cl_3$ or chloroform, and also to $C_2Cl_4$, perchloride of carbon. Thus, instead of regarding chloroform as a compound of the imaginary radical formyle, it may be looked upon as derived from protocarburet of hydrogen; for $C_2H,Cl_3$ has a formula similar to $C_2H,H_3$.

CHLOROFORM, $C_2H,Cl_3$. Besides being formed as just stated, it occurs in many reactions; thus hydrated chloral in the presence of alkalies is resolved into formic acid and chloroform. Chloroform, however, is always prepared by the action of the alkaline chlorites upon alcohol, acetone, or wood spirit. It is best obtained by heating together alcohol, bleaching powder, and water. The proportions used vary. About 1 part of pure alcohol with 6 or 7 parts of bleaching powder and 20 of water appear to answer very well. The theory of the process is not very clear; formic acid and formic ether are produced, and probably chlorate of lime. The product is distilled into a receiver containing water, it is then well washed, and then dried by being allowed to remain for some time in contact with chloride of calcium; it is then distilled from its own weight of sulphuric acid. It is a well known fragrant liquid of sp. gr. 1·5, boils at 142°. It should not colour oil of vitriol when mixed with it, and when allowed to evaporate on the hand should not leave an unpleasant smell. If it contains alcohol, when crystals of bichromate of potass are put into it, and sulphuric acid added, the crystals will tinge the surrounding liquid green.

Chloroform is not very combustible. It is soluble in alcohol, insoluble in water. It has a remarkable power of dissolving many substances, as phosphorus and camphor.

BROMOFORM is prepared in a similar manner, and is a liquid very analogous to chloroform.

IODOFORM, $C_2HI_3$, Is prepared by mixing together a solution of iodine in alcohol with a solution of caustic potass or the carbonate, until the iodine

solution is nearly decolourised. On heating this, and allowing the liquid to cool, the iodoform is deposited in crystals mixed with some iodide of potassium. The crystals are to be purified by washing and re-solution in alcohol. The iodoform is deposited from the alcoholic solution in brilliant yellow lamellas. Iodoform is soluble in alcohol, and insoluble in water. It has a very peculiar odour, is volatile a little above 212°. At a higher temperature it is decomposed into carbon, iodine, and hydriodic acid.

*Perchloride of Carbon* $C_2Cl_4$, is formed when a current of chlorine is passed into a retort containing chloroform. The retort is exposed to sunlight, and then gently heated, and the product of the distillation again exposed to a current of chlorine. This is repeated several times. The liquid is shaken with mercury to remove excess of chlorine and again distilled. It is a liquid of sp. gr. 1·59, boils at 172°.

*Acetone,* (pyroacetic spirit), $C_3H_3O$, is prepared by heating together two parts of sugar of lead, and one of powdered lime, and distilling in an iron retort. The product is first rectified from chloride of calcium, then left for some time in contact with chloride of calcium. It is then distilled over chloride of calcium, and this is repeated if necessary until a liquid is obtained, which boils at 100°. The formation of acetone is due to the resolution of acetic acid into acetone and carbonic acid; for $C_4H_3O_3 = CO_2 + C_3H_3O$.

Acetone is a clear liquid of a penetrating smell and taste. Its sp. gr. is 0·79. It is soluble in water, alcohol, and ether.

Acids produce interesting reactions with acetone. Sulphuric acid may be taken as an illustration. When acetone is mixed with this acid, heat is disengaged, the mass becomes brown, and sulphurous acid escapes. If water is then added, and the whole is neutralised by carbonate of lime or baryta, a compound of sulphuric acid, lime or baryta, and a substance of the formula $C_6H_5O$, termed mesitic ether, is formed, because it is supposed to be the oxide of mesityline, the imaginary radical of acetone, which would then be the hydrate of the oxide of mesityline, and analogous to alcohol. This ether can be procured by mixing equal quantities of acetone and sulphuric acid, cooling the mixture, and then adding two volumes of cold water, the mesitic ether swims upon the top, and can be drawn off and purified by distillation from lime.

Cacodyle, $C_4H_6As$ (Alkarsine). When a mixture of acetate of potass and arsenious acid is distilled, a fetid liquor is obtained of spontaneous inflammability. The formation of this substance may be attributed to a reaction between arsenious acid and protocarburetted hydrogen, by which some of the oxygen of the former, and some of the hydrogen of the latter, unite to form water. Thus $C_4H_8 + AsO_3 = C_4H_6AsO + 2HO$. The fetid liquor is the oxide of cacodyle.

Cacodyle itself is best obtained from the chloride, by heating it with zinc, which retains the chlorine and sets the cacodyle at liberty. Cacodyle is a clear fluid, which crystallises when cooled to 20°. It boils at 338°. It sinks in water, is spontaneously inflammable, of most offensive smell, and very poisonous.

*Oxide of Cacodyle*, $C_4H_6AsO$, is obtained by purifying the product of the distillation of acetate of potass, and arsenious acid, by redistillation in an atmosphere of carbonic acid. It is then rectified from lime or barytes.

In is an ethereal liquid, possessed of considerable refrigerating powers, sp. gr. 1·762, boils at 302°, becomes solid at 13°, forming white scales. It has a strong disagreeable smell, and is very poisonous. In the air it smokes and burns. It is insoluble in water, but kept under it for some time it forms cacodylic acid. It dissolves phosphorus, sulphur, and iodine, and takes fire in chlorine. It dissolves in some acids and forms salts. The salts of several metals are reduced by it to the metallic state.

*Cacodylic Acid*, $C_4H_6AsO_3,HO$. This acid is produced whenever the oxide is made to pass into a higher state of oxidation. The action of red oxide of mercury under water will easily effect this change. This acid forms transparent crystals,—oblique equilateral prisms ; soluble in water and alcohol. It has no odour and is not poisonous, unless injected into the circulation. It has a very feeble action on bases.

*Chloride of Cacodyle*, $C_4H_6AsCl$. When a weak solution of bichloride of mercury is poured into a solution of oxide of cacodyle in weak alcohol, an abundant white compound is formed, which is to be dissolved in boiling water and purified by repeated crystallisation. It is a compound of bichloride of mercury, and oxide of cacodyle. When this is distilled with hydrochloric acid, a chloride of cacodyle is formed, some free oxide of cacodyle comes over with it.

It is an ethereal liquid, boiling at 212°, spontaneously inflammable, and with a very disagreeable smell. It is a most powerful irritant. It is very slightly soluble in water and ether, but soluble in alcohol.

Other compounds of cacodyle, such as the sulphuret, cyanide, &c. may be formed.

VII.—OTHER PRODUCTS DERIVED FROM THE HYDROCARBURRETTED ALIMENTS, BY A FERMENTATION WHICH IS NOT THAT OF ALCOHOL.

The formation of lactic and butyric acids takes place under circumstances where the fermentation appears directed under the influence of an alkali or lime. For instance, by taking curdled milk, whose coagulum consists of a combination of lactic acid and caseum, and adding solution of bicarbonate of soda, the lactic acid is taken up by the soda, and every addition of the soda causes the formation of fresh quantities of lactic acid. Many animal substances, fats and cheesy substances, produce this kind of fermentation in saccharine substances; nor is it easy to see what precise limits separate the formation of lactic from that of butyric acid.

LACTIC ACID, $C_6H_5O_5,HO$. Besides the sources already described, lactic acid is found in the watery infusion of nux vomica after it has been kept some time, in the acrid juices of many roots, in rice water, in several other vegetable sources, and in the urine, milk, gastric juice, &c. Lactic acid can be formed from the fermentation of any hydro-

carburetted aliment in contact with an albuminous principle. The acid is to be saturated with chalk added to the fermented liquor, the lactate of lime evaporated until it crystallises, and then decomposed by oxalic acid. The easiest process seems to be to dissolve 14 parts of cane sugar in 60 of water, and then add 4 parts of old cheese and 7 of chalk. The whole is to be maintained at a temperature of between 78° and 86°, until a large deposit takes place of crystals of lactate of lime; some mannite is also formed; the lactate should be purified by re-solution in boiling water and crystallisation. After the lime is precipitated as oxalate of lime, the lactic acid remains in solution. The solution must be concentrated by evaporation in a water bath. It then forms a syrupy liquid which may be further purified by solution in ether, and evaporation of the solution. There are several other processes.

Lactic acid is a colourless syrupy liquid of a very acid taste, which mixes in all proportions with water and alcohol. Sp. gr. 1·25.

When heated above 266° it loses an equivalent of water, and there remains a solid fusible bitter substance, almost insoluble in water, but soluble in alcohol and water, and which, exposed to air and moisture, gradually regains its former state. When heated above 450°, it begins to be decomposed, and yields several products, as carbonic acid and carbonic oxide, citracic acid, aldehyde, and two substances pass over by distillation—one a light oil, which has the composition $C_{10}H_8O_4$, and is called lactone; and another crystallisable substance which separates in rhombic tables on evaporating the product, and whose formula is $C_6H_4O_4$, called *lactide*, which represents lactic acid deprived of its water.

*Lactone* is best prepared by distilling the products of the distillation of lactic acid, and stopping the distillation when the temperature reaches 266°. The distilled liquid is then to be washed with small quantities of distilled water, one portion is dissolved in the water, another floats on the top: this is lactone, which is to be dried over chloride of calcium and distilled. It is a colourless liquid, which is darkened by exposure, and has an aromatic smell with a hot taste. It is lighter than water, boils at 197°, and burns with a blue flame. Lactic acid has the power of dissolving a considerable quantity of freshly precipitated phosphate of lime. It coagulates white of egg, dissolves in milk without alteration, and coagulates it when heated.

*Lactic Acid in the Animal Body.*—Lactic acid exists as an immediate principle in the bodies of animals; it also exists there in the form of lactates of potass, soda, and lime.

Lactic acid can be separated from the tissues, solids, and liquids of the body by the following process, applicable to muscular flesh. Meat separated from fat is to be cut very fine, then macerated in cold water and well pressed; the liquid is then to be heated in order to coagulate albumen, treated with a little baryta in order to neutralise the acid, then evaporated to the consistence of a syrup. Creatine crystallises at the end of some days. The mother liquor is then to be evaporated a little; by the addition of a little alcohol, the nitrates of baryta and potass crystallise. The portion which remains fluid is completely

evaporated and extracted by alcohol; the solution is left at rest until some crystals form. The liquid then contains hardly anything but lactates of potass or baryta. The alcoholic solution is treated with oxalic or sulphuric acid to precipitate the baryta and potass. The liquid is then treated with ether as long as there is a precipitate. The alcohol and ether are driven off, and the acid saturated with milk of lime. The mass is then treated with a mixture of ether and alcohol, which dissolves the pure lactate of lime; on evaporating the solution the lactate of lime is obtained, which can be decomposed by oxalic acid. The best test for lactic acid is the characteristic form of the crystals of lactate of lime. These are in needles or tufts parting from a common centre (see fig. 45). It is soluble in boiling alcohol, and crystallises on the cooling of the liquid. The lactates generally are not possessed of very characteristic properties.

*Butyric Acid*, $C_8H_8O_4$, or $C_8H_7O_3,HO$. When the fermentation of saccharine substances has passed a certain limit, as has been stated, after the formation of lactic acid, that of butyric acid begins. It may be produced by mixing 50 parts of sugar with 4 or 5 of acid and 25 of chalk, and 3 or 4 times as much water added to the mixture. At a temperature between 78° and 80° the fermentation goes on, and if sufficiently prolonged, goes beyond the lactic to the butyric. After some weeks the liquid contains only butyrate of lime. This liquid is distilled with a little muriatic acid. A mixture is distilled over, which is composed of butyric acid, with a little muriatic and acetic acids. It is left in contact with chloride of calcium, and the butyric acid floats at the top. What floats on the top is then removed and distilled in a retort furnished with a thermometer. What passes over at first is watery; but at 327° only butyric acid is distilled over. Butyric acid can also be obtained from butter. It is an oily fluid, which is soluble in alcohol, ether, and water. It boils at 314°. At a temperature of — 4° it crystallises in plates. It forms salts called butyrates.

When dry butyrate of lime in small quantity is distilled, the product consists chiefly of *butyrone*, a substance which is supposed to be an oxide of an imaginary radical, *butyryle*. The formula of butyryle is $C_8H_7$, and of butyrone $C_8H_7O$. Butyrone is a transparent oil of sp. gr. 0·83, and boiling at 284°·5, and possessed of a burning taste. *Butyral* is the hydrate of the oxide of butyryle. It is a colourless liquid, of a penetrating odour. It boils at 203°, has a sp. gr. of 0·82.

## VIII. MANNITE, $C_6H_7O_6$.

The conditions of fermentation under which mannite is produced are not very well ascertained; but they appear to require a high temperature (86°). Mannite occurs in several vegetables, especially in the manna which is collected chiefly from incisions in the *fraxinus ornus*. Manna contains 60 per cent. of mannite. It is best obtained from manna by the action of boiling alcohol, on the cooling of which crystals of mannite form. These crystals are to be washed with cold alcohol, and then dissolved in boiling spirit, and

crystallised from the solution. If the mannite be accompanied with sugar, this may be destroyed by fermentation with yeast. When crystallised in this way from alcohol, mannite forms anhydrous quadrangular prisms, which are colourless and transparent. It has a sweet taste, is soluble in cold water, very much so in hot, and less in cold alcohol. It is converted by nitric acid into oxalic and oxysaccharic acids. In many of its reactions with alkaline and earthy bases, mannite closely resembles sugar. From what has been said, it follows that it is unfermentable.

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## SECTION III.—FATTY BODIES. ELEMENTS OF NUTRITION.

FATS are somewhat naturally characterised by the appellations *suet,* or tallow, butter, and oils. They are solid and fluid, but those of them in the former condition are easily melted. In many animals the fat is fluid. This is especially the case in cold-blooded animals. In all animals when the cellular tissue containing the fat is exposed to the temperature of boiling water, being immersed in it, the fat is melted, escapes from the cells containing it, and floats on the top of the water. In plants, the fat occurs chiefly in the seeds. Although the depôts of fat are not so considerable as in animals, yet there are some seeds which contain large quantities of oil, as the castor-oil plant, which contains 62 per cent. The presence of oil in the seeds especially has been supposed to have an important relation to their germination. In that process the seed gives off carbonic acid, and absorbs oxygen, as in the respiration of animals. In vegetables, the oil is diffused in drops through the cells. The general solvent for fatty bodies is ether; and it furnishes the best chemical means for extracting them.

Fatty bodies are known by the following general characters—by their sweetness, smoothness, and unctuosity; their easy fusibility, lightness, being lighter than water, and their combustibility and volatility or destructibility by heat. They are either colourless or slightly yellow. All the natural fatty bodies undergo more or less change, when it is attempted to distil them. At a high temperature above 572°, they boil: fatty substances of a different nature from the original principle, various liquid or solid carburets of hydrogen, inflammable gases, and carbonic acid, are produced, along with a substance of very fetid odour, named *acroleine.* The volatile oils, that is to say, those which can be distilled without alteration, are entirely different from the fixed oils; none of them is nutritive, but all are more or less medicinal.

When oils are exposed to the air, they either become rancid, or they dry, and form on a substance a coat or varnish; the latter are what are termed the drying oils. The latter class is principally composed of vegetable oils. The fatty substances of the more solid character are more like the oils which have a tendency to become

rancid than the drying oils. The rancidity of oils is accompanied with an absorption of oxygen, and a disengagement of carbonic acid and hydrogen. At the ordinary temperature of the atmosphere, some fatty substances show a tendency to spontaneous combustion, and, if mixed with spongy platinum, and a current of oxygen is directed on them, burn at a temperature below that of boiling water, giving rise to the formation of carbonic acid and water. The presence of albuminous matters accelerates the oxidation of fatty substances, and their rancidity. This is, therefore, an approach towards a species of fermentation. This rancidity is owing to an acidification of the fatty principles, and may be obviated more or less by the presence of an alkaline carbonate,—by the neutralisation of this principle by the alkali. The nature of the changes which fatty principles undergo, in many cases spontaneously, is shown by the transformation of palm oil when exposed to air and moisture. It contains a principle called palmitine, $C_{70}H_{66}O_8$, which added to 6HO, is equal to $2(C_{32}H_{32}O_4)$, or two equivalents of palmetic acid, and $C_6H_8O_6$, or an equivalent of glycerine, a thick syrupy oleaginous principle.

### Action of Acids and Bases on Fatty Principles.

Sulphuric acid at first rather attacks the foreign principles of fatty oils : hence it is sometimes used to purify them. In greater quantity it separates their glycerine and combines with it. When a mixture of oleine and margarine is acted on, compounds of sulphuric acid with these substances are formed, themselves of an acid character. Nitric acid solidifies fats, and causes oleine to be changed into eleadine, a solid fat.

When alkalies are boiled along with fatty substances, they give rise to the substances called soaps. If the solution be not too concentrated, the soaps are found in the form of more or less soluble compounds of the fatty acids of the fats previously existing or formed by the agency of the alkali, to the exclusion of the glycerine. On concentrating these, and employing pressure and a high temperature, the soap becomes more solid, and can be formed into moulds. In this process, the coagulation of the soap is often promoted by the addition of sea-salt to the liquid.

The soaps formed by lime and baryta are insoluble in water. This is one of the reasons why hard water is so unfit for washing purposes. Soaps differ according to the various fatty acids with which the alkali is combined in them.

Metallic oxides possess somewhat similar properties as bases to the alkalies and earths, as regards the fatty acids, but with them are formed the compounds known as plasters ; so that we find these three classes of compounds of fatty acids and bases characterised generally by the properties of the base; the alkaline by their solubility ; the metallic, like those of mercury and lead, by their fusibility.

Oils dissolve phosphorus and sulphur.

Liquid fats are the best solvents of solid fats. Most fats consist of a liquid and solid substance. In examining most of them at a low

temperature,—for example, olive oil at a temperature approaching the freezing point,—they are found to contain a solid, granular body floating in the liquid. This, at the ordinary temperature, had been dissolved in the more fluid part. The action of alcohol and other solvents, resembles that of the more fusible part of the compound fat on the solid part. Thus human fat, dissolved in boiling alcohol, leaves on cooling a solid substance, which is only fusible at 104°. The fat exhausted both by alcohol and ether of the principles they can remove, leaves a substance fusible only at 140°. The more fusible oily portion being retained by the alcohol, this difference in the fusibility of fatty substances furnishes the great means of separating them. Thus in the suet of different animals a substance is found insoluble in cold alcohol, and very slightly soluble in hot alcohol, but very soluble in boiling ether, and whose melting point is 140°. This principle has received the name of stearine. It marks the highest limit of the fusibility of the natural fats. The most fluid part of the animal fats and vegetable oils is a substance which remains liquid below 32° ; is very soluble in hot or cold alcohol, and which is termed oleine. A principle intermediate between these, soluble in alcohol and ether, fusible at 104°, is termed margarine. These principles, in the act of saponification, are disposed to separate into an acid and glycerine. Whatever may be the variety of fat acids produced by the saponification of the natural fats, they all agree in the production of glycerine.

The fat acids can all be referred to a basic form, $C_2H_2$. Thus we have margarie, acid $C_{34}H_{34}O_4$; caproic, $C_{12}H_{12}O_4$; butyric, $C_8H_8O_4$, &c.

The fats may be treated under the following heads. 1st, glycerine : 2nd, stearine ; 3rd, modifications of these principles by sulphuric and nitric acids ; 4th, natural fatty bodies and principles which result from them.

## I. Glycerine, $C_6H_8O_6$, or $C_6H_7O_5+HO$,

Is best prepared by boiling olive oil, with litharge and water; the fat acids forming not a soap, but insoluble lead plaster, with the litharge, and glycerine being dissolved in the water. Any lead in the water is separated by passing a stream of sulphuretted hydrogen through it. The solution of glycerine is then concentrated in a water bath. Glycerine is a thick yellowish syrup, without smell, of a sweet taste; it is insoluble in ether, and unites in all proportions with alcohol and water. Its sp. gr. is 1·28. It can be heated to 300°, without being decomposed. When heated more strongly it becomes black, and is decomposed, yielding some undecomposed glycerine by distillation, and several volatile products; amongst other, acroleine: it takes fire when heated in the air. Its reactions with bases resemble much those of sugar. It dissolves several bases, as oxide of copper and the earths, and these then resist the action of carbonic acid. Sulphuric acid and peroxide of manganese change it into carbonic and formic acids. It unites with sulphuric and other acids, forming new acid compounds. When a dilute solution of glycerine is mixed with yeast, and kept for some months at a temperature between 70° and 86°, gas is disengaged; and acetic and formic acids, with an acid

called *metacetic*, are formed. Glycerine is more similar, in many respects, to the saccharine than the fatty series. If we suppose in glucose the substitution of 2 atoms of oxygen by 2 of hydrogen, we get the formula of glycerine.

Making glycerine twice the atomic weight above given, we get $C_{12}H_{14}O_{14}$ (glucose)$-2O+2H=C_{12}H_{16}O_{12}=$glycerine.

*Acroleine*, $C_6H_4O_2$, or $C_4H_3O+HO$ (*hydrate of the oxide of acryle*), is prepared by distilling a mixture of glycerine and anhydrous phosphoric acid in a current of carbonic acid gas. The distilled liquor consists of three layers, of which the upper contains the acroleine. The products are then digested for some time in a close vessel in contact with oxide of lead, then distilled over chloride of calcium, and anew distilled at a temperature below 125° in carbonic acid. Acroleine is a volatile, oily fluid, possessed of strong irritating and asphyxiating properties. It is soluble in ether and water. It reduces oxide of silver; detonates, with potass and nitric acid, forming a resinoid product. When it acts under water in the cold upon oxide of silver, it forms an acid called *acrylic acid*, which combines with the oxide, and can be separated by sulphuretted hydrogen.

In order to obtain the acrylic acid pure, after it has been separated from the oxide of silver, by SH, the solution must be saturated by carbonate of soda, the soda salt decomposed by sulphuric acid and distilled, the distilled product neutralised by oxide of silver, and again decomposed by sulphuretted hydrogen. Acrylic acid is a colourless liquid, of agreeable smell, and acid taste. It is very similar to acetic acid, to which, by its formula $C_6H_3O_3,HO$, it is closely related, and into which it readily passes.

## II. Stearic, Margaric, and Oleic Acids, with the Substances whence they are Derived.

Stearine, the natural combination of glycerine and stearic acid, is found in all the suets in different animal and vegetable fats, and in the bile. It is purified by pouring the essence of turpentine on the suet in fusion. On cooling there is formed a solid deposit, which is to be expressed and treated a second time with essence of turpentine. The solid matter is to be taken up by boiling ether, and is deposited, on cooling, in white brilliant pearly plates, inodorous and tasteless. Stearine melts at a temperature a little above 150°, and on cooling forms a solid pulverable mass. It is insoluble in water, soluble in 7 or 8 parts of boiling alcohol, most soluble in boiling ether. Stearine may be regarded as a stearate of the imaginary radical glyceryle.

*Stearic Acid*, $C_{34}H_{33}O_3,HO$, is obtained from the saponification of suet by earths and alkalies. Suet may be saponified by lime, and the stearate of lime decomposed by dilute boiling sulphuric acid. The oleic acid, formed at the same time, may be separated by expression; and the stearic acid separated by repeated solution in boiling alcohol and crystallisation. Stearic acid crystallises from its solutions in brilliant needles, which are brittle; it is solid up to 250°, according to some; sp. gr. 1·01. It is insoluble in water, soluble in its own

weight of alcohol and ether, and reddens litmus. Heated in air, it burns like wax : hence its use in forming candles. When oxidated, it passes into margaric acid.

It can be distilled in vacuo ; but in the air it is decomposed, furnishing water, carbonic acid, margaric acid, and other products. Stearate of potass may be prepared by dissolving stearic acid with an equal weight of hydrate of potass dissolved in 20 parts of water. A granular substance is produced, which is to be expressed and dissolved in boiling alcohol ; on cooling, brilliant white plates of the stearate are deposited. Stearic acid may be made to form an ether, like most fat acids.

*Margaric Acid*, $C_{32}H_{33}O_3,HO$.—Margarine, which bears the same relation to margaric acid that stearine does to stearic acid, is perhaps the principle most extensively found in fatty matters. It is obtained by repeated crystallisation of human fat from solution in alcohol. It is regarded as the margarate of the oxide of glyceryle.

*Margaric Acid.*—When stearic acid is boiled for a short time in nitric acid, the mixture on cooling leaves a mass which, being expressed, and well washed with alcohol, and then dissolved in boiling alcohol, leaves crystals of margaric acid. It is generally obtained by saponifying human fat or olive oil, and precipitating the soap by acetate of lead. A precipitate is thus obtained, which is a mixture of margarate and oleate of lead. The oleate of lead may be removed by ether : the margarate of lead remains undissolved. The margarate of lead is to be treated with weak hydrochloric acid and strong alcohol, when chloride of lead remains, and margaric acid dissolves and may be obtained by careful evaporation.

Margaric acid is very soluble in pure alcohol and ether, insoluble in water. At the temperature of 572°, it may be distilled without decomposition. The principal difference between it and stearic acid is in its point of fusion, which is 140°.

*Margarone*, $C_{33}H_{33}O$, is obtained by distilling one part of lime and four parts of margaric acid, and purifying the product. It is a white pearly substance, whose fusing point is 171°. This substance has been termed the oxide of margaryle, the imaginary radical of stearic and margaric acid.

*Margaromide*, so called, is an ammoniacal soap, of which ammonia and margaric acid are the constituents.

*Margarate of potass* is obtained by a process analogous to that for obtaining the stearate.

*Oleic acid*, $C_{36}H_{33}O_3,HO$.—Oleine represents the more fluid part of fatty substances, as margarine and stearine represent the more solid parts. It is obtained by boiling lard or tallow in alcohol, until it is all dissolved. The spirit is to be reduced by distillation to an eighth of its bulk, then water is added, the oleine floats at the top ; on cooling, its separation from the solid principles is complete. Oleine is a colourless fluid, insoluble in water, soluble in alcohol and ether. Oleine is without smell, but has a sweetish taste. It crystallises in needles, at 13° or 14° below the freezing point of water. It is also called oleate of the oxide of glyceryle.

*Oleic acid* is obtained by saponifying with potass olive oil at a temperature not above 50°, displacing the fat acids by tartaric acid, decanting, washing, and digesting them in a salt-water bath with half their weight of oxide of lead. After standing some hours, the mixture is to be treated with twice its volume of ether, and allowed to rest for twenty-four hours. The ethereal solution of oleate of lead is decanted and decomposed by dilute muriatic acid. The ethereal solution of oleic acid is then decanted, and the ether evaporated. The oleic acid is washed and is nearly pure, except that it contains some products of oxidation. To separate them, the acid is saturated with ammonia, dissolved in water, and precipitated by chloride of barium. The oleate of baryta is to be washed, dried, and treated with boiling alcohol, which dissolves the more oxygenated oleate of baryta, and allows the more pure oleate of baryta to separate on cooling. This is to be purified by more than one solution and crystallisation in alcohol; finally, the oleate of baryta is to be decomposed by a solution of tartaric acid in boiling water, when the oleic acid floats at the top. It is then to be washed with cold boiling water, at 32°.

Oleic acid crystallises from its solution in alcohol when cooled to a little above the freezing point in long white needles. These melt at 57°. It is then an oily, colourless liquid, without taste or smell. It does not redden litmus; it rapidly absorbs oxygen from the air. It is insoluble in water, soluble in alcohol and ether; it readily dissolves other fatty substances. Sulphuric acid colours oleic acid. Nitric acid has a powerful action on oleic acid, and produces many acids from it. When treated with nitrous acid—not in excess—it is transformed into a crystalline substance isomorphous with it, termed *elaidic acid.*

*Oleophosphoric* acid, a compound of oleic acid with phosphorus or phosphoric acid, may be obtained from the brain by dissolving it in hot ether, from which compounds of cerebric and phosphoric acid separate on cooling. The residue is to be dissolved in boiling alcohol, acidulated with sulphuric acid; on cooling, and treating the extract and residue with cold ether, the oleophosphoric acid is in solution, and may be obtained by evaporation. It is more viscid and coloured than oleic acid; insoluble in water, but in boiling water it swells a little. Long boiling with water and alcohol, or the contact of azotised matters, transforms it into a matter identical with oleine. Bases transform it into oleic and phosphoric acids and glycerine. In all probability it has never been obtained pure or free from cerebric acid. It contains 2 per cent. of phosphorus.

The concentrated alkaline solutions decompose oleic and claidic acids with disengagement of hydrogen and acetic acid, and a peculiar fatty matter is formed. With more weak lyes it forms soaps, also with earths and metallic oxides, similar to the analogous compounds of the other fat acids.

### III. Action of Sulphuric and Nitric Acids on Stearine, Margarine, Oleine, and their Compounds.

When sulphuric acid acts upon stearine it resolves it into an acid

called sulphoglyceric, and leaves the stearic acid without acting upon it. With vegetable oils it forms sulpholeic and sulphomargaric acids. The sulphomargaric acid is soluble in water, and is decomposed by ebullition, or even spontaneously, into three acids, the metamargaric, the hydromargaritic, and the hydromargaric, which differ from each other in the quantities of water they respectively contain. Similar acids are formed with oleine, and from them two substances can be obtained, termed *elaene* and *oleene*, of peculiar properties.

Nitric acid converts stearic acid quickly into margaric acid; but its action upon oleic and margaric acids is of a much more complex character. Oleic and margaric acids disappear in nitric acid, furnishing a great number of new products; some of these are found in the products of distillation, others in the residual solution in the acid. Those which are volatilised belong to the series of fat acids, and form a most beautiful series of organic compounds. They all depart from the base $C_2H_2$, and maintain the same quantities of oxygen. Taking acetic acid for the commencement, we have $C_4H_4O_4$, or $C_4H_3O_3,HO$. Then we have the following series :—

| | | | | |
|---|---|---|---|---|
| Acetic acid | . | . | . | $C_4H_4O_4$ |
| Acetonic acid | . | . | . | $C_6H_6O_4$. |

Then follow butyric, valerianic, caproic, œnanthylic, caprylic, pelargonic, and capric, $C_{20}H_{20}O_4$, every one of the series in succession rising by the addition of $C_2H_2$ to the formula of its predecessor. And as formic acid has been obtained by the action of nitric acid on stearic acid, and its formula is $C_2HO_3+HO$, we may take it $C_2H_2O_4$ as the commencement of this series of volatile acids derived from the action of nitric acid on fatty acids.

The acids which remain in the nitrous solution seem to be formed by the successive addition of $C_2H_2$ to the formula $C_4H_2O_8$, which is that of oxalic acid. Thus we have, one of the series being omitted :

| | | | | |
|---|---|---|---|---|
| Succinic acid | . | . | . | $C_8H_6O_8$ |
| Lipic acid | . | . | . | $C_{10}H_8O_8$ (?) |
| Adipic | . | . | . | $C_{12}H_{10}O_8$ |
| Pimelic | . | . | . | $C_{14}H_{12}O_8$ |
| Suberic | . | . | . | $C_{16}H_{14}O_8$ |

and then an omission and

| | | | | |
|---|---|---|---|---|
| Sebacic | . | . | . | $C_{20}H_{18}O_8$ |

*Succinic acid.*—Succinic acid is obtained by distilling amber; empyreumetic oils pass over. These are put upon a moist filter, and the aqueous liquid which passes through is evaporated to crystallisation, and purefied by repeated solution and crystallisation. It is also obtained by dissolving amber in nitric acid, or by dissolving the succinic acid out of the amber by ether. When margaric acid is destroyed by nitric acid, a mixture of succinic and suberic acids remains in the acid solution. The suberic acid crystallises first. The mother water, and

the water with which the suberic acid is washed, are then concentrated
and crystals of suberic acid are obtained. These are to be dried, and
treated with cold ether, which dissolves any remaining suberic acid.
The succinic acid is then to be sublimed. Its sp. gr. is 1·55. It
fuses at 356°, and boils at 473°, but rises in vapour much earlier. It
crystallises in rhombic prisms. It loses one equivalent of water when
heated: distilled very often it loses two. It is soluble in 24 parts of
cold, and 2 of boiling water. It combines with sulphuric acid in the
proportion of one equivalent to two of the latter. It forms succinates
and bisuccinates. Its most important salt is the succinate of ammonia,
which is used to precipitate iron, in separating it from manganese.
A substance called succinamide is obtained from succinic ether by
ammonia.

Of the other acids mentioned, the suberic and sebacic are the most
important.

*Suberic Acid* may be prepared by the action of nitric acid on cork
and various barks; but it is most abundantly procured from the action
of nitric acid on stearic and margaric acids. The solution in this acid
is to be reduced one half, and then left alone for twenty-four hours.
The suberic acid is found crystallised in the form of little hard crystals,
which dry into a brilliant white powder. They are redissolved in
boiling water, and purified by distillation. Suberic acid fuses at be-
tween 122° and 130°, and loses an equivalent of water; after this, it
does not fuse, but sublimes as an oil, which solidifies in needles; it is
soluble in hot alcohol, and hot and cold ether.

The alkaline suberates are soluble in water; the suberate of am-
monia has no action on the chlorides of the alkaline earths, unless
alcohol be present, when suberates of the bases are formed.

*Suberone*, $C_8H_7O$, is a colourless strongly aromatic substance, ob-
tained by distilling suberic acid with lime.

*Sebacic Acid* is obtained by the dry distillation of an oily matter
containing much oleine in an earthenware retort, and exhausting the
distilled matter with boiling water. Solution of sugar of lead is then
poured into the lixivium, and a white flaky precipitate falls, which is
to be collected on a filter, washed, and dried. The sebate of lead is then
to be decomposed by sulphuric acid, diluted with 5 or 6 parts of water.
The whole is then heated to 212°, filtered, and the sebacic acid crystal-
lises on cooling of the liquid. Sebacic acid has a sp. gr. when fused of
1·317. It melts at 277°. It crystallises in brilliant white scales or
needles. It reddens litmus. Its salts are analogous to those of most
of the fat acids. It forms an ether.

*Pimelic Acid* crystallises on evaporation of the solution after the
suberic acid has been removed. *Adipic acid* is obtained from the
mother liquor, after the deposit of suberic and pimelic acids. This
evaporated deposits a mixture of adipic and *lipic* acids : these are dried
and dissolved in hot ether, the ethereal solution allowed to evaporate
to a half; the first granular deposit is adipic acid; the last deposit is
lipic acid. Proper means are employed to separate these more com-
pletely. They both form salts.

IV. On the Natural Fatty Bodies and Principles which
RESULT FROM THEM.

The suets, the solid fatty matters found around the kidneys and intestinal canal of several quadrupeds, yield much stearic acid; the fat of the goat yields an acid called *hircic*. It is doubtful how far hyrcine, which is analogous to oleine, obtained from the fat of the goat or sheep, is a separate principle, and whether hircic acid differs from valerianic. *Adipocere* obtained from corpses, is a soap formed by the acids of human fat, and a compound of oleic and margaric acids with ammonia, and lime, and magnesia. Lard, when it becomes rancid, contains a volatile fat acid—the caproic. The oils of fish and whales contain a fat acid analogous to the valerianic acid, and termed *phocenic*. Phocenine is a combination of glycerine with phocenic and oleic acids. Cod-liver oil is said to contain a peculiar fatty principle, called *gadueine*. It also contains oleic and margaric acids, acetic and butyric acids, iodine, bromine, and phosphorus in combination, a biliary resin, sulphates and phosphates of lime, magnesia, and soda. Butter is the oily matter which is diffused through milk in the form of emulsion. When the milk stands some time, these rise to the top, forming cream. By the operation of churning, these are completely separated from the rest of the milk, and gathered together. Butter contains three fatty principles, *butyrine, caproine*, and *caprine*, compounds of acid fats with oily substances. In order to obtain these fatty principles, purified butter is kept for some time at a temperature between $60°$ and $70°$. The oleine and the compounds of the volatile fatty acids with glycerine (butyrine, &c.) remain liquid, while the margarine remains solid, so that the liquid part can be decanted. The solid part may be purified by repeated solution and crystallisation. The fluid part is treated with anhydrous alcohol, which is left in contact with it at a temperature of $68°$ for some hours. The alcohol is evaporated by a water bath; it leaves an acid oil, consisting chiefly of butyrine. If this is saponified, and then decomposed by tartaric acid, an aqueous liquid separates. This and the washings of the acid fats are distilled. The product of the distillation, saturated by caustic barytes, is then evaporated by a gentle heat, the residue reduced to powder, and left in contact with $2·77$ times its weight of water for twenty-four hours. The portion which remains undissolved is treated with the same proportion of water, and this is repeated until only a little carbonate of baryta remains. The products of these digestions are allowed to evaporate spontaneously, so that the more soluble salt may be separated from that which is less so. The first which separates is the caprate, then the caprylate, and lastly the caproate of baryta. These salts decomposed by sulphuric acid give their respective acids. *Capric acid*, $C_{20}H_{19}O_3,HO$, or $C_{20}H_{20}O_4$, crystallises in fine needles at $52°$. It is insoluble in water, soluble in alcohol, possessed of a bitter taste. *Caprylic acid* has the formula $C_{16}H_{15}O_3,HO$. It solidifies at a little below $53°$. It is slightly soluble in boiling water. It has a somewhat disagreeable smell and taste. *Caproic acid*, $C_{12}H_{11}O_3,HO$, is a limpid oily liquid, which has a smell like sweat, or vinegar. It is very acid, and blisters the tongue. All

these acids form ethers. Vaccinic acid appears to be a compound of capric and butyric acids. Wool well washed with distilled water yet contains two fatty principles, which it is very difficult to saponify, stearerine and elaierine. *Cerebric acid* is obtained by making an alcoholic extract of the dry brain, and treating the extract with cold ether, which dissolves the oleophosphoric acid, and leaves the cerebric. The cerebric acid may be crystallised from boiling alcohol or ether. It then forms white crystalline grains; but these examined by the microscope are discovered to be amorphous. When boiled in water, it swells up like starch. Many vegetables yield oils containing peculiar fatty acids, as the *cocculus indicus*, the *anamirtic acid;* palm oil, the *palmitic;* the butter of nutmegs, myristic acid; the benic acid from oil of ben ; lauric acid from laurel oil.

Castor oil is a natural oil somewhat remarkable for its chemical properties. Castor oil has sp. gr. of 0·9699 at 53°. When exposed to the air it becomes rancid. It is distinguished from all other oils by two properties. First it is soluble in all proportions in absolute alcohol, which distinguishes it from all the drying oils, to which class it belongs; and it is solidified by sulphurous acid, which distinguishes it from all known oils. Nitric acid also acts on it differently from the other drying oils,* solidifying it, and forming a substance called palminc. When castor oil is saponified, three fatty acids are formed, *stearoricinic*, or *margaritic, ricinic*, and *oleoricinic*, or *elaiodic*. The first of these separates at 62° from the oily mass of castor oil-soap of potass or soda, decomposed by hydrochloric acid. It is expressed between folds of blotting paper, then dissolved in concentrated boiling alcohol, on the cooling of which it crystallises in pearly scales. It is very soluble in alcohol, and may be partly sublimed without decomposition. The ricinic acid is separated after the removal of the stearoricinic by means of a cold a few degrees below the freezing point ; the third acid remains fluid.

When castor oil is distilled at a temperature of 518°, it separates into 2 parts, a colourless spongy residue, which remains in the retort, and a volatile part which passes into the receiver. The product is composed of water with some acroleinic, ricinic, and oleoricinic acids, and an aromatic matter, which has been termed œnanthole, or œnanthylic aldehyde.

*Œnanthole*, hydrous oxide of œnanthyle, $C_{14}H_{14}O_2$, is obtained by taking the oily part of the product just described, and distilling it several times with water ; then neutralising with barytes, which separates it from the acids with which it is associated, finally distilling it and collecting the product when the temperature of the retort rises to above 312°. It is then dried by chloride of calcium. It is a colourless, highly refractive fluid, with a strong penetrating aromatic odour, and a sweet sharp taste; it boils at 314° ; it is very soluble in alcohol and ether, hardly so in water. It forms a crystallisable hydrate with water. In contact with oxygen it becomes œnanthylic acid; chromic acid inflames it, and it reduces nitrate of silver like acetic aldehyde.

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* Linseed oil is one of the best known drying oils.

*Palmine*, $C_{37}H_{34}O_6$ is a white substance, intermediate between wax and resin, formed by the action of nitric acid and other substances on castor oil.

*Palmic Acid*, $C_{34}H_{32}O_5HO$.    When castor oil is saponified, and the soap decomposed by muriatic acid, and then diffused through dilute nitric acid, and a current of nitrous acid passed through, a waxy mass is formed, which, dissolved in alcohol, yields acicular crystals of the above formula.

*Œnanthylic acid*, $C_{14}H_{13}O_3,HO$, is prepared by treating castor oil with twice its bulk of nitric acid, diluted with its bulk of water, and distilling.    The oily matter which passes over is distilled with water, and the product dried upon vitrified phosphoric acid.  It is a colourless, transparent liquid, of a sugary, aromatic, and sharp taste.   It is very little soluble in water ; mixes readily with alcohol and ether ; boils at 299° ; burns with a somewhat smoky flame. Its compound with potass is a kind of jelly.   Some of its salts are crystallisable.   It forms an ether, the œnanthylic.

*Œnanthic acid*, $C_{14}H_{13}O_2,HO$.   The oily liquid which passes at the end of the distillation of brandy is a mixture of œnanthic acid and œnanthic ether.   The mixture is boiled with carbonate of soda, when the ether swims on the surface of the liquid ; the alkaline œnanthate is then decomposed by a mineral acid.   The solution of the œnanthate, concentrated and hot, being decomposed, the œnanthic acid swims on the surface of the liquid.   It boils at 144° ; is a brilliant white substance like butter, without smell or taste ; at a higher temperature it is a reddish oil, which reddens litmus and saturates alkalies.   It is insoluble in water, but readily soluble in alcohol, ether, and wines. When heated it loses water.   It boils at 500°.

*Œnanthic ether*, $C_4H_5O,C_{14}H_{13}O_2$, may be prepared by heating œnanthic acid with sulphovinate of potass, or by distilling the oils of wine lees with carbonate of soda to remove acid, and then over chloride of calcium.   It is a colourless fluid of a vinous odour, and its vapour when respired speedily stupefies.   Its taste is strong and disagreeable. It is very soluble in alcohol and ether, sp. gr. 0·842.   This ether is supposed to be the principle to which the bouquet of wines is owing.

*Pelargonic acid* is an acid fat obtained from the *pelargonium roseum.*   It forms an ether, which is supposed to give the peculiar flavour to whisky.   *Ceradoic acid* is obtained from ceradilla; and *rocellic* and *lichenstearic* acids from lichens.   A fatty matter termed bog-butter is obtained from peat.

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### SAPONIFICATION.

The process of saponification consists essentially in the displacement of glycerine, the hydrate of the oxide of glyceryle, an imaginary radical, from its combination with a fat acid, and the substitution of a base, alkaline, earthy, or metallic, for the oxide of glyceryle in its combination with the acid.  Soaps are of very different, and sometimes complex composition, as regards the fat acids they contain, which may

easily be conjectured from the vast variety of animal and vegetable fats now used in their manufacture.

Those fats which contain much stearine and margarine, give the more solid soaps, as far as the fat acids are concerned. Much oleine renders the consistence less, and the vegetable drying oils, linseed, &c., softer still. The only soluble soaps are those with potass, soda, and ammonia. Soaps are coloured mostly by means of salts of iron and copper, introduced during the period of saponification. Soaps contain from 25 to 60 per cent. of water. Soaps of potass are much softer and more soluble than soaps of soda. The long continuation of soap in water has a tendency to promote the separation of its principles; excess of the fat acid and the alkali precipitates, and excess of alkali remains in the water. Solution of muriate of soda boiled with soap causes it first to disperse in gelatinous flocculi, which on the cooling of the liquid collect into a compact mass. The essential part of the process of soap-making is exceedingly simple. It consists in introducing the oily matter into a lye of alkali and lime, boiling it there for a certain time, and then solidifying the soap in frames, using various substances either to harden and consolidate the soap in the process of boiling, or to colour it. The sp. gr. of most soap is little above that of water, 1·032. When exposed to the air new soap loses water.

## CHAP. II.—BODIES ANALOGOUS TO ALCOHOL, AND THEIR DERIVATIVES.

THE compounds included under this head might almost have been included in the preceding chapter; but as some of them could not be so included, and on account of their importance, they are placed apart.

Alcohol produced from the fermentation of sugar has a close relation to acetic acid. Substituting two equivalents of oxygen for two equivalents of hydrogen in alcohol, we get the formula of acetic acid, $C_4H_6O_2 - 2H = C_4H_4O_2$, and adding $2O$, · we get $C_4H_4O_4$, or $C_4H_3O_3, + HO$. Palmetic acid is obtained from ethal, called also cetylic alcohol, by a formula similar to that by which we get acetic acid from alcohol, viz., the removal of two equivalents of hydrogen, and their replacement by two of oxygen. The formula for ethal is $C_{32}H_{34}O_2$; by the same addition and subtraction we get $C_{32}H_{32}O_4$. Again, phocenic or valerianic acid is derived in precisely the same way from fruit oil, oil of potatoes, or amylic alcohol, and formic acid in the same way from wood spirit.

This remarkable analogy places ethal, the oil of potatoes, and wood-spirit beside the fatty principles.

An alcohol may be defined, an organic volatile substance, liquid or solid, which loses one equivalent of water to produce an ether, two equivalents of water to produce a hydro-carburet of the formula $C_n H_n$, which loses two equivalents of hydrogen to form an aldehyde, and which

loses two equivalents of hydrogen, and acquires two equivalents of oxygen to form an acid of the class already described.

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### SECT. I.—ETHALIC ALCOHOL AND ITS DERIVATIVES.

ETHALIC ALCOHOL, $C_{32}H_{34}O_2$, or $C_{32}H_{33}O,HO$; Cetylic Alcohol (hydrate of the oxide of cetyle).

*Spermaceti, or Cetine.*—The ethalic compounds are chiefly derived from spermaceti, but can also be obtained from palm oil and oleic acid. It is probable that perfectly pure spermaceti is ethalic aldehyde, $C_{32}H_{32}O_2$. It is also termed cetine. It is obtained by allowing the oil procured from the head of the cachalot to remain for some time exposed to the air, when a crystalline substance separates. This is expressed, and digested with the aid of heat, with a solution of caustic potass. A soapy blackish scrum is formed, which is removed. The limpid oil which remains is washed with boiling water, and transferred into crystallising vessels, and on cooling the spermaceti crystallises. By repeated solution in alcohol, it is brought to its state of greatest purity and a constant melting point. Spermaceti is a solid, crystalline, colourless substance, almost without taste and smell, melts at 120°, inflammable, quite insoluble in water, soluble in hot alcohol and ether, soluble also in essential and fatty oils; distilled at 680 it is resolved into ethalic acid and ethaline; and fused with potass, it is converted into ethalate of potass and ethalic alcohol.

*Ethalic Alcohol,* $C_{32}H_{33}O,HO$ (Cetylic Alcohol, Hydrate of the Oxide of Cetyle), is obtained by melting two parts of spermaceti, and adding by degrees, continually stirring, one part of pieces of hydrate of potass. When the matter is solidified, it is dissolved in water, and hydrochloric acid immediately added. Ethal and ethalic acid liquefied by the heat float as an oil on the surface: this oil is heated with potassa, water, and hydrochloric acid. The oily mixture again obtained is saponified by slaked lime. Ethalate or cetylate of lime is formed, and the ethal is separated by absolute alcohol. It is redissolved in ether, which on evaporating leaves it perfectly pure.

Ethal is a colourless insipid solid, which crystallises on the cooling of its alcoholic solution, in brilliant plates, and melts at 118°; is volatile and inflammable, insoluble in water, and very soluble in alcohol and ether. When distilled with perchloride of phosphorus, it forms the substance called chlorethalic ether.

*Ethaline,* $C_{32}H_{32}$ (Cetene), is obtained by distilling ethal repeatedly from anhydrous vitrified phosphoric acid. It is a colourless oily liquid, which boils at 527°. It is insoluble in water, soluble in alcohol, neutral, without taste, very inflammable.

*Ethalic Acid,* $C_{32}H_{32}O_4$. It is called also cetylic and palmitic acid. Combined with glycerine, it forms palmitine, which exists in

palm-tree oil, in other natural fats, and forms the fatty matter of coffee. Ethalic or cetylic acid may be obtained from the compound which it forms with lime in the preparation of ethalic acid. Potassa is heated along with the ethalate of lime; after the mixture has ceased to give out gas, it is put into water, and saturated with hydrochloric acid; and the flocculi which separate are put into a boiling solution of barytes in excess. The whole is evaporated to dryness, any ethal separated by alcohol, the ethalate of baryta decomposed by ether, and the ethalic acid dissolved in ether. Ethalic acid is a colourless, insipid solid, lighter than water, in which it is insoluble, very soluble in alcohol and ether, burns at a temperature approaching 500°, melts at about 132°, and on cooling forms a mass of brilliant needle-like crystals. When it burns, it is partly transformed into a new acid, the *palmitonic*, $C_{31}H_{30}O_3,HO$.

### SECT. II.—AMYLIC ALCOHOL AND ITS DERIVATIVES.

AMYLIC ALCOHOL, $C_{10}H_{12}O_2$. Hydrate of the Oxide of Amyle, $C_{10}H_{11}O,HO$.—This series is much more numerous than the compounds of cetyle; and, in point of fact, there is hardly one of the compounds of the true alcoholic series that cannot be represented in the series of the compounds of amyle.

The products of alcoholic fermentation are accompanied with a peculiar oil, lighter than water, and insoluble in that fluid, and much less volatile even than water, and which is possessed of a very disagreeable smell and taste. This, called fusel oil, oil of whisky, and oil of potatoes, consists chiefly of amylic alcohol. In the distilleries of whisky, and such like spirits, it is found that the residues of the stills in which the spirit is rectified contain a large quantity of this substance. By distilling these residues a milky liquid is obtained, which, after some time, deposits amylic alcohol. This impure product is shaken with water; the oil swims on the top, is decanted, and distilled, until the boiling point reaches 269°. The receiver is then changed, and the product collected, and again rectified. It is an oily, colourless, very fluid liquid, of a strong smell, and hot acrid taste. It boils at the temperature above stated, sp. gr. 0·8, freezes at —4 in leaf-like crystals; is hardly soluble in water, but much more so in alcohol and ether, fatty and essential oils, and acetic acid; and dissolves sulphur and phosphorus. Exposed for a long time to the air, amylic alcohol undergoes oxidation, and valerianic acid is formed. Exposed to the action of chlorine, it absorbs that gas, and forms a substance called *chloramilal*. Amylic alcohol absorbs hydrochlorine acid gas, and by repeated distillation gives rise to chloramylic ether.

AMYLE, Ayl, $C_{10}H_{11}$, has been obtained by the action of zinc on iodide of amyle. Is an oil which boils at 311°. It is the supposed basis of the amylic compounds.

AMYLIC ETHER, $C_{10}H_{10}O$, is prepared by heating in a closed vessel, up to 212°, a solution of chloramylic ether, in an alcoholic solution of potass. It is a liquid of an agreeable odour, which boils at 230°.

A most extensive series of etherial compounds of amyle with acids exists, the formulas of which may be gathered from that of amyla-cetic ether, $C_{10}H_{11}O, C_4H_3O_3$. The ethers, with chlorine, bromine, and iodine, sulphur, and cyanogen, have the addition of 1 eq. of the halo-genous principle or element to 1 of amyle. Amyle also forms com-pounds with several acids, as the amylotartaric, the amylosulphuric acids.

*Amylic Mercaptan*, $C_{10}H_{11}S, HI$, is prepared by the reaction of the hydrosulphate of sulphuret of potassium dissolved in alcohol upon chloramylic ether, in a close vessel. It is a colourless oily liquid, possessed of a very considerable refrigerating power, and of a pene-trating odour, like onions, boils at 241°, sp. gr. 0·825.

*Amyline*, $6_{10}H_{10}$ (*Valerine*). — All the reagents which withdraw water from ordinary alcohol act in a similar way upon amylic alcohol. Several acids have this power, but especially chloride of zinc, and anhydrous phosphoric acid. By repeatedly distilling oil of potatoes with this last-named substance, there is at last obtained a colourless fluid, with an odour like putrid cabbage. *Paramyline* and *Melamyline* are isomeric with valerine, but have different properties.

AMYLIC OR VALERIANIC ACID, $C_{10}H_{10}O_4$, or $C_{10}H_9O_3, HO$; termed also Dephinic, Phocenic and Valeric Acid, may be obtained by several processes. This acid constantly results from the extreme oxidation of fats and oils. It exists in combination with glycerine in the oils of the whale, dolphin, skate, and cod. It is found in certain plants, especially in valerian and angelica roots. It is chiefly obtained from amylic alcohol, valerian root, or whale oil. One part of oil of pota-toes, and ten parts of caustic potass are heated together in a chloride of zinc bath, to above 352° and towards 400°, for some hours. Hy-drogen and carburetted hydrogen are disengaged. The mass is to be allowed to cool in a stoppered flask, which is to be opened under water. The mass is to be well washed with water, saturated with excess of sulphuric acid, and then distilled. The product is acid. It is to be saturated with soda, and the valerianate of soda, evaporated to dry-ness, is to be decomposed by phosphoric acid. The valerianic acid dis-tilled from the mixture forms an oily layer on the surface of the fluid in the receiver.

Valerianic acid is obtained from valerian root, by macerating it powdered with water, sulphuric acid, and bichromate of potass, in a retort for twenty-four hours, and then distilling, neutralising the product as before with soda, and distilling with sulphuric and phos-phoric acid.

Amylic acid is a colourless oily liquid, with a strong odour of valerian. It has a sharp acrid taste, and blisters the tongue; sp. gr. 0·937. It boils at 347°. It is somewhat soluble in water, quite so in alcohol, acetic acid, and ether. The amylates or valerianates are, for the most part, soluble, with the exception of those of silver and

copper. Their taste is at first styptic, then sweet. When the alkaline and carthy salts are distilled, amylic aldehyde is produced. When valerianic acid is poured into a solution of acetate of copper, and the mixture shaken, oily drops of amylate (valerianate of copper) are formed, which, the agitation being continued, are converted into a bluish green crystalline powder. This character distinguishes valerianic from butyric acid, which at once throws down from the solution of acetate of copper a whitish blue precipitate.

*Valerone, Valeral, Amylic Aldehyde,* $C_{18}H_{18}O_2$, may be obtained by distilling the valerianate of baryta with a strong heat, and redistilling the product, or by distilling valerianic acid with excess of lime. It is a limpid colourless liquid, which boils at 212°; the sp. gr. 0·820. It has a hot taste and penetrating odour. It is soluble in all proportions in alcohol, ether, and essential oils. Burns with a bright flame. Oxydising bodies transform it into valerianic acid. This change may also be effected in contact with air, by the action of spongy platinum.

*Valyle, or Butyle,* $C_8H_9$, is produced in the decomposition of valerianic acid by galvanism. It is an oily fluid, boiling at 226°. It is regarded as analogous to ethyle, methyle, &c.

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SECT. III.—METHYLIC ALCOHOL AND ITS DERIVATIVES.

METHYLIC ALCOHOL, $C_2H_3O,HO$.—Numerous products are formed during the distillation of wood, and amongst others a fluid known as wood spirit, pyroligneous ether, and hydrate of the oxide of methyle, and wood naphtha. The compounds of methyle, however, differ from the alcoholic series in possessing no aldehydes, nor carburetted hydrogen, isomeric with bicarburetted hydrogen; but in all its other relations the analogy with alcohol is so exact, that wood spirit may be ranked among the alcohols. The following series will show the mode in which the methyle compounds are formed. Putting out of view the alleged radical methyle, whose title to be the basis of the methyle series has been contested, we have—

| | | | | |
|---|---|---|---|---|
| Methylic alcohol | . | . | . | $C_2H_4O_2$. $C_2H_3O$, HO. |
| Methylic ether | . | . | . | $C_2H_3O$. |
| Chloride of methyle | . | . | | $C_2H_3Cl$. |
| Methylic or formic acid | | . | | $C_2H_2O_4$. $C_2HO_3$,HO. |

And so forth. Now, in the first of these compounds, the carbon and hydrogen appear in the relation of protohydruret of carbon; and in two of the others, as the chloride and oxide, one eq. of an electro-negative element replaces one of hydrogen. In others of the methylic series, the carbon and hydrogen show the relation of light carburetted hydrogen.

*Methylic Alcohol*, is found in the watery part of the distillation of wood spirit. This fluid is distilled a second time; and only the first tenth of the product is collected. This, rectified several times from quicklime, or by adding an excess of chloride of calcium to the crude product, and heating in a water-bath as long as volatile matters are disengaged, then adding to the residue a volume of water equal to that of the wood spirit employed, and continuing to heat, the combination of the wood spirit and chloride of calcium is destroyed by the water; and continuing the heat, pyroxylic spirit is distilled.

Methylic alcohol is a colourless fluid, possessed of a peculiar sharp aromatic and alcoholic odour. It burns in the same way as alcohol, and is readily soluble in water, alcohol, and ether. It dissolves sulphur, phosphorus, fatty bodies, resins, and many salts. Its sp. gr., when pure, is, according to some, 0·798; according to others, 0·813: boils between 140° and 150°. It undergoes oxidation slowly in the air; but spongy platinum oxidates its vapour, rapidly forming formic acid. When distilled with peroxide of manganese and sulphuric acid, formic acid and *methylal* are produced. Caustic potass converts it into formic acid. With sulphuric acid it forms sulphate of methyle, which when heated yields oxide of methyle in the gaseous form. Nitric acid produces formic acid and nitrate of methyle. Chlorine forms with it oily compounds of uncertain composition. Chloride of lime produces chloroform with it in large quantity. It combines with perchlorides of tin, iron, and antimony; and by distillation yields chlorides of methyle. With chloride of calcium it forms a compound which may be crystallised in hexagonal tables.

METHYLE, $C_2H_3$, Me, is obtained by the action of zinc on the iodide of methyle, in a sealed tube, at 302°. It is also obtained by passing a galvanic current through a solution of acetate of potass, when methyle appears at the positive pole. Methyle is a gas of sp. gr. 1·0365. It cannot be condensed at a high pressure, and is still gaseous at zero of Fahrenheit. It burns with a bluish flame. Chlorine combines with it under the influence of light, and without condensation. It forms hydrochloric acid, and a gas $C_4H_5Cl$. Methyle forms compounds with several bodies. It displaces an eq. of hydrogen in ammonia, and forms a compound with amidogen, $NH_2C_2H_3$, *methylamine*. In like manner it displaces hydrogen from phosphorus.

METHYLIC ETHER, $C_2H_3O$, is obtained by distilling equal volumes of strong sulphuric acid and wood spirit—methylic ether, carbonic and sulphurous acids are disengaged. The gas is passed through milk of lime; with this the gas combines, or rather is absorbed by it, and, on heating it, is disengaged, and must be collected over mercury, and dried and purified by pieces of caustic potass. It is a colourless gas, with a strong and pleasant etherial odour—inflammable. Sp. gr., 1·6; is not liquefiable at 3°.

*Chloride of Methyle*, $C_2H_3Cl$, is produced by the action of sulphuric acid and chloride of sodium on pyroxylic spirit; it is an etherial inflammable gas. Iodide of methyle is a volatile liquid obtained by the

distillation of pyroxylic spirit, phosphorus, and iodine, or by the reaction of hydriodic acid upon pyroxylic spirit.

Methylic ether absorbs chlorine, and forms several compounds in which the hydrogen of the methyle is replaced by chlorine, according to the extent to which the action is carried, until at last all the hydrogen is replaced by chlorine, and a compound is obtained of the formula $C_2Cl_3O$, called the perchloride of methylic ether. It is a fluid of sp. gr. 1·594, which boils at 212°, and has a strong suffocating odour. The chloride of methyle and chlorine exposed to the intense light of the sun form first $C_2H_2Cl_2$, in which one equivalent more is substituted for one of hydrogen of methyle; it is a very volatile liquid, termed chloride of methyle. A further dose of chlorine produces chloroform, and the ultimate result of the action of chlorine on chloride of methyle, under the most intense solar light, is perchloride of carbon, $C_2Cl_4$.

*Methylal*, $C_6H_8O_4$, is prepared by distilling from one part of pyroxylic spirit with an equal weight of peroxide of manganese and $1\frac{1}{2}$ of sulphuric acid. The first portion of the product is repeatedly rectified over chloride of calcium until the distilled liquid boils at $107\frac{1}{2}°$. Methylal is an aromatic, agreeably smelling liquid; sp. gr., 1·8551. It is soluble in three parts of water, in every proportion in alcohol, ether, and pyroxylic spirit. An alcoholic solution of potass converts it into formic acid; so do nitric and sulphuric acids, and bichromate of potass. By the action of chlorine on it, sesquichloride of carbon is formed.

*Sulphite of the perchloride of carbon* is formed by the action of aqua regia on bisulphuret of carbon. It is a white, crystalline, volatile body, with a characteristic penetrating odour, and much the appearance of camphor, and having the formula $2(SO_2),C_2Cl_4$. When this compound is treated with solution of potass, and gently heated until neutralisation is effected, a salt is formed of the formula $2(SO_2),C_2Cl_3O,KO$. If a reducing agent, as protochloride of tin, metallic zinc, &c., is brought into play, the sulphite of perchloride of carbon is transformed into an acid, and becomes $2(SO_2),C_2Cl_2HO,HO$, forming with potassa $2(SO_2),C_2Cl_2HO,KO$; and the influence of galvanism produces other compounds. The sulphuret of methyle, and cyanide of methyle correspond with the chloride.

### ACID COMPOUNDS OF OXIDE OF METHYLE.

*Sulphate of Oxide of Methyle*, $C_4H_3O,SO_3$, is procured by distilling one part of pyroxylic spirits with eight or ten parts of sulphuric acid. It is an oily liquid with a garlicky odour. Methylo-sulphuric ether boils at 370°; sp. gr. 1·324. Alkaline solutions decompose it, forming the methylo-sulphuric acid. Boiling water also decomposes it, forming the sulpho-methylic acid, $HO,C_2H_3 2SO_3$, a crystalline substance. When the neutral sulphate is heated with chlorides, cyanides, &c., etherial compounds are formed of methyle and the halogenous principle. Ammoniacal gas acts with disengagement of heat upon the sulpho-methylic ether. It converts it into a soft mass, from which a

crystalline substance is obtained, called sulphomethylane. It contains an acid termed *sulphamidic*, $NH_3S_3O_9$. The formula for sulphomethylane is $C_2H_5NS_2O_6$.

*Methylo-sulphuric acid* is soluble in all proportions in alcohol and water, and forms perfectly defined salts, which, by dry distillation, yield methylo-sulphuric ether.

Many etherial compounds of methyle exist besides those mentioned. Their nature may be conceived from the formula $C_2H_3O,NO_5$, for methylo-nitric ether; $C_2H_3O,C_2O_3$, methyloxalic ether, &c. In fact oxide of methyle replaces the water of hydrated acids like other bases.

*Oxalate of Oxide of Methyle*, $MeO,C_2O_3$. This ether of methyle may be particularly selected. It is prepared by distilling a mixture of one part of wood spirit, one part of anhydrous oxalic acid, and an eighth of concentrated sulphuric acid. The whole product is redistilled, and towards the end of the distillation more wood spirit is added. The ether is precipitated from the product by water. It should be redistilled with oxide of lead to separate any oxalic salt. It is a solid crystalline substance which melts at 124°, and boils at 322°. It is very soluble in alcohol and wood spirit, and separates from its solutions in rhombic transparent plates.

*Cyanate of Oxide of Methyle*, $C_2H_3O,NC_2O$, is obtained by distilling cyanate of potass with the acid sulphomethylate of potass. It is a volatile liquid which possesses a peculiar smell. It yields a crystalline compound with ammonia of the same composition as urea, except that for 1 eq. of hydrogen, one of methyle is substituted. It may also be procured by passing cyanic acid into pyroxylic spirit. When this ether is treated with potash the following action takes place:

$$C_2H_3O,NC_2O + KOHO + HO = 2CO_2KO + C_2H_3,NH_2, \textit{Methylamine}.$$

# CHAP. III.—WAXY SUBSTANCES.

Waxy substances bear an obvious external resemblance to fatty bodies, and also in some faint respects they resemble the alcohols. They contain carbon and hydrogen in nearly equal (equivalent) proportions, but little oxygen. When waxy matter is destroyed by the action of nitric acid, the volatile acids of fatty substances, the margaric, succinic, pimelic, &c., make their appearance. By distillation margaric acid is produced along with carburets of hydrogen isomeric with olefiant gas, with a mixture of paraffine and disengagement of carbonic acid, characters which place the waxes near fatty bodies.

Waxes are produced from two sources; some by bees, and such like insects; others are found on leaves and other vegetable productions,

as dust or varnish. They give to the parts of vegetables which they cover a shining aspect, and probably render them impervious to moisture.

Waxes may be somewhat loosely divided into two sections. First, those which contain 80 or upwards of carbon, and not more than eight or nine of oxygen in the 100, and whose melting point does not exceed 158°. These may be regarded as the waxes properly so called. Secondly, those which have a smaller proportion of carbon, about 74 per cent., and whose oxygen may amount to 14·5, and whose point of fusion descends as low as 122°.

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### SECT. I.—WAXES PROPERLY SO CALLED.

Bees' wax washed and fused, or bleached by exposure on grass to the sun and moisture, is white, and slightly translucent, without smell or taste, sp. gr. 0·960—0·966; hard at the freezing point of water, malleable at 86°, fluid at 155°. Boiling alcohol separates it into three portions,—*myricine*, the insoluble part; 2nd, *cerine*, the soluble part, which is deposited by the alcohol on cooling in fine needles; and, 3rd, *ceroleine*, soluble in cold alcohol, and which, therefore, remains in solution. Cerine forms from 70 to 90 of the wax, ceroleine only 4 or 5 per cent. The distillation of wax produces neither acroleine nor sebacic acid. At first an acid water passes over; then a solid colourless matter; then an oily liquid, loaded with leafy crystals; and there remains in the retort a black residuum, which is elastic, insoluble in alkalies, and which, heated further, furnishes a volatile liquid, and leaves a carbonaceous residuum. Carbonic acid and olefiant gas are disengaged during the operation.

The solid products of the distillation consist of margaric acid and paraffine; the liquid product is a mixture of carburets of hydrogen of unequal volatility, and of the same composition as olefiant gas. Their boiling point rises as high as from 278° to 428°. Distilled with lime, wax yields a large quantity of yellow oil, composed of principles of unequal volatility, and towards the end of the distillation, paraffine especially is obtained.

*Cerine, Cerotic Acid*, $C_{54}H_{54}O_4$. Cerine is the part of bees' wax soluble in alcohol; it fuses at a little above 161°; it is nearly pure cerotic acid. Cerotic acid is obtained by precipitating a boiling alcoholic solution of cerine when hot by sugar of lead, and filtering while hot. The precipitate is to be purified by solution in ether and alcohol, and decomposed by acetic acid; the precipitate is to be washed with boiling water, and filtered while hot. The cerotic acid is deposited on cooling. Chinese wax contains cerotic acid, along with oxide of ceryle or cerotyle, $C_{54}H_{55}O$; and when this wax is fused with caustic potass,

the result washed with water, and solution of chloride of barium added, and the precipitate treated with alcohol or ether, *cerotine*, the alcohol of *cerotyle*, is dissolved, its formula being $C_{54}H_{55}O,HO$, while ceratate of baryta is left behind. It is a crystalline substance. Cerine is soluble in 16 parts of boiling alcohol. Cerotic acid is in granular crystals, and volatile without decomposition when heated by itself. It melts at between 172° and 174°.

*Myricine*, compound of palmitic acid and melissine.

Myricine remains after the cerine has been dissolved. It requires 200 parts of boiling alcohol, and 99 parts of cold ether to dissolve it. It is deposited from the alcoholic solution in white flocculi. It melts a little above 143°.

*Melissine* (melissic alcohol), $C_{60}H_{61}O,HO$, is obtained by saponifying myricine with potass, decomposing the soap with an acid, and dissolving the melissine out by hot alcohol and crystallising. It forms silky crystals, which melt at 185°. When melissine is heated with a mixture of potassa and lime, and decomposed with a dilute acid, it yields *melissic acid*, which is separated by crystallisation from alcohol. Its formula is $C_{60}H_{59}O_3,HO$. It melts at 191°.

Melissine forms a resinous substance with chlorine.

*Ceroleine* is a soft substance, soluble at 86°, very soluble in alcohol and ether, and reddens litmus; it seems to be somewhat similar to oleine. Its ultimate analysis gives C, 74; H, 12·51; O, 8·75; which is very similar to that of oleine.

China wax, sinesine, is a crystalline vegetable wax, brought from China, which in appearance closely resembles spermaceti. The wax of canes is very similar to it.

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## SECT. II.

The principal waxes belonging to this class are, 1st, one extracted from cork by the action of alcohol and ether, and which crystallises in needles, termed suberine, and which, on being treated by nitric acid, yield an acid termed adiposuberic or ceric; 2nd, a wax obtained by boiling in water the leaves of myrica cerifera, but which is rather a fat, since it saponifies with formation of the ordinary fat acids; 3rd, similar substances from other species of myristica. The leaves of the cabbage and many other plants give also principles whose nature is so anomalous that it is difficult to say whether they should be regarded as fats, waxes, or resins.

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## CHAP. IV.—ORGANIC COMPOUNDS OF AMMONIA AND CYANOGEN

May be divided into two sections. 1st, those which do not owe their origin solely to physiological sources ; and 2nd, those which do so.

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### SECT. I.—COMPOUNDS NOT DERIVED SOLELY FROM PHYSIOLOGICAL SOURCES.

Several of these have been spoken of under the head of inorganic chemistry for the sake of convenience, although they belong to the class of organic bodies more particularly.

When they are obtained from animal products, it is by such processes as the following. First, when animal matters are distilled in close vessels, they leave behind a carbonaceous matter of great value for deodorising purposes, and a liquid is distilled over. This liquid separates into two layers, the superior containing several oily matters ; the inferior consisting chiefly of solution of carbonate of ammonia. This is filtered several times through a bed of powdered sulphate of lime. During the filtration a double decomposition takes place, and the greater part of the ammoniacal salt is converted into sulphate, and the decomposition is completed with sulphuric acid. The sulphate is crystallised out and converted into muriate by decomposition of its solution with muriate of soda. It is crystallised and purified by sublimation. Second, putrefying urine is heated in a large iron kettle by steam, and a quantity of slaked lime introduced sufficient to displace all the ammonia, which is then collected in sulphuric or muriatic acid, which condenses it. Thirdly, by a similar process ammonia may be separated from the condensed liquid of tar works.

The changes which take place when organic ammoniacal salts are heated have been already referred to.

When oxalate of ammonia is distilled, carbonic oxide, carbonic acid, ammonia, and cyanogen are given off, and white flocculi form at the top of the retort, to which the name of *oxamide* has been given. This sublimate contains some carbonate of ammonia, from which it can be freed by washing. The composition of oxamide is $C_2O_2NH_2$, or rather $C_4O_4NH_2$. Oxamide is a white pulverulent substance, without taste or smell, and without action on test paper. Oxamide is melted and volatilised by heat, and partially decomposed cyanogen, prussic acid, and urea are formed, also some paracyanogen, which remains with carbon in the retort. Oxamide is almost insoluble in cold water, slightly soluble in hot, and is deposited from the solution in crystalline plates ; when oxamide is exposed to the action of concentrated acids, especially with the aid of heat, it reforms oxalate of ammonia. It is the type of the amides.

*Oxamic Acid,* $C_4O_4NH_2,HO_2$, or $C_2O_2NH_2,C_2O_3HO$ (oxalate of

oxamide), is obtained by heating the binoxalate of ammonia in an oil bath at 446° until it becomes yellow. A yellowish mass remains in the retort, from which oxamic acid is extracted by cold water. The solution is then precipitated by baryta or lime; oxalic acid is thus separated as insoluble oxalate of baryta or lime; and the oxamic acid remains. The oxamate of lime or baryta is then decomposed by sulphuric acid; and the oxamic acid is separated from the remaining solution by slow evaporation, as a powder. Oxamic acid forms compounds with several of the etherial principles.

*Formiamide.*—This name has been given to prussic acid obtained in a particular way, to indicate its relation to the amides. When formiate of ammonia, $NH_3HOC_2HO_3$, is heated it is resolved into $NC_2H + 4HO$.

*Compounds of Cyanogen.*—PARACYANOGEN, isomeric with cyanogen, $NC_2 (N_6C_{12})$, is best obtained by heating the cyanide of silver; cyanogen is disengaged, but paracyanide of silver is likewise formed, and remains in the retort as a gray mass. When this is treated with nitric acid, the silver is in great part dissolved, and the paracyanogen remains with some silver; it is washed and dried, then treated with strong sulphuric acid which dissolves the whole; the paracyanogen is precipitated by the addition of water, and is to be washed and dried. Paracyanogen is a black substance, tasteless and inodorous, not volatile, insoluble in water and alcohol. The alkalies and muriatic acid dissolve it. It is oxidated by nitric acid, which produces a yellow acid, a compound of 3 eqts. of cyanogen, with 1 of oxygen, which has been termed paracyanic acid.

*Compounds of Cyanogen and Oxygen.*—The cyanic acid has been already spoken of. When gaseous chloride of cyanogen is condensed by the pressure of its own vapour, and the tube is immediately broken, it escapes instantly; but if left for some days, before the tube is broken, nothing escapes—but crystals are found to have been formed, surrounded with an oily liquid. These crystals melt at 284°, and are volatile at 374°. This solid chloride may also be formed by exposing dry prussic acid in a flask of chlorine to the action of the sun's rays. When this solid chloride of cyanogen is digested in water, it is resolved into muriatic acid, and a solid compound of oxygen and cyanogen isomeric with cyanic acid, $C_2N,Cl + HO = C_2NO + ClH$. It has been regarded as solid cyanic, or cyanuric acid. *Cyanic acid,* $CyO,HO$, may be obtained in the anhydrous state by distilling cyanuric acid, $Cy_3O_3,3HO$, which separates into three eqts. of cyanic acid, and condensing the product in a freezing mixture. It is a volatile, fluid, acrid acid, which, when removed from the freezing mixture, boils, and leaves a dense white solid characterised by no remarkable properties, insoluble in water, alcohol, and acids, and which on being heated is converted into cyanic acid, and is termed cyamelide.

*Fulminic Acid,* $Cy_2O_2$, has not been isolated. Fulminates of silver and mercury are obtained by treating mercury or silver with an excess of nitric acid and alcohol—1 of mercury dissolved in 12 of aqua fortis (sp. gr. 1·36), and 11 of alcohol added, or one of silver,

a violent reaction takes place, and numerous gaseous products are given off. In the end, a white or grayish powder remains, the fulminate of mercury, or minute crystalline needles, the fulminate of silver. The following is supposed to be the reaction which takes place, not taking into account the gases disengaged:—

$$C_4H_6O_2 + \quad 2NO_3,AgO = N_2C_4O_2,2AgO+6HO.$$
$$\text{Alcohol.} \quad \text{Nitrate of silver.}$$
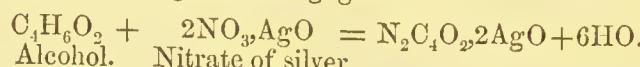
The nitrate being first reduced to nitrite.

*Cyanuric Acid*, $C_3O_3,3HO$, is obtained by heating urea. Urea is a compound of cyanic acid and ammonia. When heated, its ammonia is driven off, and three eqts. of cyanic acid coalesce to form one eq. of cyanuric acid. Cyanuric acid is also obtained by other processes, shortly to be referred to. Cyanuric acid is a weak acid, slightly soluble in cold water; more so with the aid of heat. Little is known of the cyanurates. When cyanuric acid is heated in close vessels it is volatilised in the form of cyanic acid, which, along with the mode in which it is formed from the cyanate of ammonia, shows with what ease, under different circumstances, these compounds of cyanogen and oxygen are changed into one another.

Cyanogen with metals forms those compound bases of which ferrocyanogen, $FeCy_3$, is an example. Similar combinations are concluded to exist with several of the metals, but none of them has been isolated. The mode in which the prussiate of potass is prepared has been already described. From it the

*Ferrocyanic Acid*, $FeCy_3+2H$, is obtained. This compound may be regarded as a compound of cyanide of iron and hydrocyanic acid, but there are reasons for giving it the above formula. It is much more acid than prussic acid; is prepared by decomposing a strong solution of ferrocyanide of potassium by a solution of tartaric acid in alcohol; cream of tartar is precipitated, and the acid remains in solution and may be separated by filtration and spontaneous crystallisation. When exposed to the air, it undergoes gradual decomposition; strongly heated, it is resolved into hydrocyanic acid and cyanide of iron.

*Ferricyanogen* is supposed to exist as a compound radical isomeric with ferrocyanogen. Its formula is $Fe_2Cy_6$; it is also called ferridcyanogen, and has the symbol Cfdy. Its hydracid, the hydroferrocyanic which is combined with three of iron, is obtained by decomposing the ferrocyanide of lead with sulphuretted hydrogen. Its principal salts have been referred to under the head of inorganic chemistry.

*Hydrocyanic Acid*, CyH, eq. 27, is also referred to in the inorganic chemistry. It may be prepared, besides the modes referred to, by decomposing prussiate of potass by sulphuric acid or cyanide of potassium, by tartaric acid, and by other processes. In the first way, 15 parts of powdered ferrocyanide of potassium and 9 parts of sulphuric acid, mixed with an equal bulk of water, are to be heated together, and the product collected in a receiver containing chloride of calcium; in the other process, solution of cyanide of potassium is decomposed by the

tartaric acid, bitartrate of potass thrown down, and prussic acid remains in solution.

In the former process the result is the formation of bisulphate of potass, an insoluble compound of cyanide of potassium and cyanide of iron, and hydrocyanic acid. Thus $2(K_2C_6N_3Fe)+3HO+6SO_3=Fe_2$ $Cy_3K+3(KO,2SO_3)+3CyH$.

Perhaps it is obtained in the strongest state by passing sulphuretted hydrogen over dry cyanide of mercury in a tube, and collecting the product in a receiver, cooled by a freezing mixture.

Hydrocyanic acid is a colourless liquid, remarkable for its physiological properties. Its smell resembles that of the peach. Its taste is acrid, and its fumes cause excessive irritation of the nostrils and eyes. It has a sp. gr., when pure, of $0·7058$ at $45°$. It boils at $79°$, and freezes at zero. It cannot long be kept in the pure form, especially when exposed to the light, decomposing into several not very well known compounds. When mixed with strong muriatic acid, it forms muriate of ammonia and formic acid.

The tests for hydrocyanic acid consist in the formation of a white precipitate with nitrate of silver, soluble when boiled in nitric acid, and which, on being heated in a tube with its open portion drawn out to a small point, gives a stream of cyanogen, which burns when ignited with a purple flame, while metallic silver is left behind. Then it gives a white precipitate with salts of copper. Then by its formation of Prussian blue with a mixture of persalt and protosalt of iron. A solution containing it is to be mixed with a little solution of copperas and some caustic potass, and hydrochloric acid is added. The object is to precipitate the oxide of iron by the potass, so that the hydrocyanic acid may act upon it; and then get rid of the excess of oxide thrown down by the potass, by dissolving it in the muriatic acid. Exposure to the air gives the well known precipitate of Prussian blue, if prussic acid be present.

SULPHOCYANOGEN, $C_2NS_2$—Cy. Sulphocyanide of potassium is prepared as described at p. 76. It is a compound of potassium with the supposed compound radical sulphocyanogen, and its abridged formula would be KCsy. It is crystallised in anhydrous prisms, which are very soluble. When the alkaline sulphocyanides are distilled with an acid they yield sulphocyanohydric acid, but it is best obtained by decomposing the sulphocyanide of lead with sulphuretted hydrogen. It is a colourless acid fluid, of a sharp smell, very poisonous, and which, as well as its compounds, gives a blood-red colour with solutions of persalts of iron. It is found in the saliva.

Mellone, $C_6N_4$. When solution of sulphocyanic acid is neutralised with ammonia, the sulphocyanide of ammonium is formed, and by evaporating this gently is obtained as a deliquescent substance; and when this is mixed with common salt, and chlorine passed over the mixture at a red heat, chloride of cyanogen and sulphur are disengaged, and a mixture of mellone and chlorides of potassium and sodium is left. By washing, the mellone is left as a gray or yellowish powder. Mellone is insoluble in water and alcohol, forms a compound with

hydrogen, and forms salts called mellonides. When sulphocyanide of ammonium is treated with muriate of ammonia, and the residue treated with hot water, a substance remains of the composition $C_{12}H_9N_{11}$, or $2(C_6N_4)+3NH_3$. It is a grayish substance, insoluble in water and alcohol, called melam. When melam is boiled in water containing potassa until it is dissolved and the solution evaporated, another compound radical separates by crystallisation. It is called *melamine*. Its formula is $C_6H_6N_6$. And in the liquid from which the melamine has crystallised out, another principle of similar properties, called *ammeline*, remains. Lastly, when ammeline is dissolved in strong sulphuric acid, it forms yet another principle,—*ammelide*.

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### SECT. II.—COMPOUNDS OF CYANOGEN WITH AMMONIA, DERIVED FROM PHYSIOLOGICAL SOURCES.

The compounds of cyanogen found in the body are compounds of cyanic acid with ammonia, or derivable from these combinations. Carbonic, oxalic, and formic acids are highly oxygenised acids; and if such acids, or compounds analogous to them, exist in the organisation, such as might be produced from oxygenisation of the aliments, it is easy to conceive how ammoniacal compounds reacting upon them might give rise to compounds analogous to those of cyanogen, oxygen, and ammonia. The source of the ammonia may be understood. It comes from the decomposition of the azotised tissues. Ammoniacal compounds are formed in the tissues, as soon as they begin to be destroyed in the processes of life, and the object to be attained in the vital process is their removal from the system.

The following formula will show the composition of some of these bodies:—

Urea, $C_2N_2H_4O_2=NC_2O+NH_3,HO$, or cyanate of ammonia, or cyanate of the oxide of ammonium.

Uric acid, $C_{10}N_4H_4O_6=2CO_2+3(NC_2H)+C_2NO,HO$, or carbonic acid, prussic acid, cyanic acid, and water.

Allantoine, $C_4N_3H_4O_3=2NC_2+3HO$, or cyanogen and water.

Xanthic oxide, $C_5N_2H_2O_2=CO_2+2NC_2H$, or carbonic and prussic acids.

*Urea*, $C_2N_2H_4O_2$ (Ur.).—Urea may be obtained from urine by evaporating this fluid to the consistence of a syrup in the waterbath, and drying it as much as possible. An alcoholic extract is then obtained by treating the urea with absolute alcohol. This is then driven off, and the residuum dissolved in water, and heated gently along with animal charcoal, and filtered through that substance. It is then heated to 122°, and as much oxalic acid added as the solution will dissolve. On the cooling of the liquid, crystals of oxalate of urea are obtained. The oxalate is treated with boiling

water and animal charcoal, and the solution filtered and concentrated until crystals are again formed. These are dissolved, and finely powdered pure carbonate of lime added, to saturation, oxalate of lime is precipitated, and urea remains in solution, and can be obtained by evaporation. It may also be formed by the direct action of cyanic acid and ammonia in solution. It may also be obtained on a large scale by heating strongly together prussiate of potass and peroxide of manganese, and treating the lixivium of the residue with sulphate of ammonia, using suitable means to extract the urea.

Urea may also be prepared by the following process:—The urine is to be evaporated to dryness by the water-bath, and the residue finally dried over sulphuric acid.* When the mass is quite hard, it is treated several times with boiling absolute alcohol, decanting off the extract every time. To the whole of the alcoholic solution, a little sulphuric ether is then added, allowing it to trickle down the sides of the vessel, avoiding a mixture of the two liquids. A precipitate appears at the meeting of the two fluids, which gradually spreads through the whole, until, at the end of 4 or 5 hours, the sides and bottom of the vessel are found studded with fine crystals of urea. More ether is then added, in the same way, as long as a precipitate is formed. If it is desired to preserve the urea thus prepared, it must be anew crystallised from water. Urea generally crystallises in long needles, or in long quadrangular prisms (see fig. 45). It is inodorous and colourless, and has a cooling taste like nitre. It is very soluble in water, less so in alcohol, and hardly so in ether; cold water dissolves its own weight of it, so does boiling alcohol. In boiling water there is not a limit to its solubility. It is neither alkaline nor acid to tests; but it combines with acids forming bodies which are regarded as salts. Urea is deliquescent in moist air, fuses at 248°, and is decomposed at a higher temperature; carbonate of ammonia, and ammonia sublime, and cyanuric acid remains. Heated with caustic soda, or potass, urea is decomposed and carbonic acid and ammonia formed. When the muriate of ammonia decomposes some of the metallic cyanates, giving rise to the formation of urea and chloride of silver.

Urea forms generally more than a third of the solids of the urine, and several hundred grains of it are daily excreted by a man. It also exists in several of the secretions and excretions, especially in certain diseases. Experiments prove that it can be formed independently of the kidneys. It is obtained from the blood by a complicated process. Urea is recognised in mixtures of it with other substances, chiefly by the appearance of its crystals under the microscope, or by this along with the destruction of the matter by heat. A little of the matter is heated on a platinum plate by a spirit-lamp. The smell of ammonia, and the sharp smell of cyanic acid, which is formed, may assist in recognising urea.

The following method is applicable as a test, and to determine the

* There is great difficulty in drying urine. In fact, the syrupy mass which remains after its evaporation cannot be dried in the open air.

amount of urea in any liquid, founded upon the fact that nitrate of mercury precipitates urea, forming with it nitrate of mercury and urea, a solution of nitrate of mercury is prepared. The quantity of this liquid requisite to precipitate a given quantity of urea is then determined. The quantity, then, of urea in any liquid deprived of albumen may be ascertained by the amount of the solution of nitrate of mercury which is used to precipitate it. Ferments, mucus, and albuminous matters rapidly convert urea into carbonate of ammonia.

*Nitrate of Urea*, $UrNO_5 + HO$, may be obtained from urine in the same way as the oxalate. Concentrated nitric acid decomposes urea. It crystallises in rhomboidal or rectangular plates (see fig. 46). Its insolubility, and the formation of these crystals, furnishes a mode of detecting urea. The liquid must be first freed of any albumen it may contain, then evaporated to a half, and treated with a little nitric acid; and after a little time the crystals deposit, and can be examined. In examining urine, this is often done on a glass plate ; and it is often sufficient, when the urea is in excess, to allow the urine to evaporate a little in the air on a glass plate, and then add a drop of nitric acid.

*Oxalate of Urea*, $Ur,C_2O_3,HO$. It has been seen how this salt may be obtained from urine. When oxalic acid comes in contact with a solution of urea sufficiently concentrated, crystals of this salt are formed of various rectangular and rhomboidal prisms. Sometimes these prisms are surmounted by pyramids; sometimes the crystals are plates. Oxalate of ammonia, when heated, fuses and boils, and ammonia is evolved with formation of cyanuric acid.

*Biuret*, $C_4H_5N_3O_4$, is obtained by heating urea for some time at a temperature between 302° and 338°, and afterwards extracting this substance from the residue. It is a white crystalline body, and is urea deprived of an atom of its ammonia. Doubling the formula of ammonia, we have $C_4H_5N_4O_4 — NH_3 =$ formula of biuret.

*Uric Acid*, $C_5HN_2O_2,HO$. (Lithic Acid).—Uric acid may be prepared by boiling the excrements of birds or serpents, which consist chiefly of it, or uric acid calculi, with caustic potass, when the uric acid dissolves. The solution is to be filtered and brought to the boiling point, and precipitated with muriatic acid, and then the crystals which form, purified by a repetition of the process. Or caustic potass in excess may be added to the solution; and the urate, which is insoluble in large excess of potass, obtained by concentrating the solution, and the urate formed, washed with dilute muriatic acid, which dissolves everything but the uric acid. It may be also prepared by adding a few drops of nitric acid to urine, or other fluid supposed to contain it, when, in the lapse of a few hours, crystals of uric acid are deposited. Uric acid is a white crystalline body, without taste or odour, but which reddens litmus. It requires 1000 parts of boiling water to dissolve it, and is insoluble in alcohol and ether, and nearly so in cold water.* Uric acid occurs as a fine white powder, or

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* The statements of the solubility of uric acid differ widely. According to some, 1720 of water at 60° dissolve it, or 1150 of boiling water. According to others, it requires 10,000 parts of cold water.

in fine prisms, very commonly in rhomboidal plates (see fig. 47). Uric acid rarely exists in the urine in the free state; but generally in the form of urates. The proportion of uric acid that can be obtained from the urine varies from 0.3 to 1 in the 1000 parts. Uric acid is somewhat soluble in muriatic acid, and more so in sulphuric. Nitric acid dissolves it, and converts it into a yellow mass, which becomes of a fine carmine on the addition of ammonia. This is the best test for uric acid. The ordinary way is to heat the supposed lithic acid, or lithate, in a porcelain capsule, with a little nitric acid; and, just on cooling, to add a drop or two of ammonia. In the action of nitric acid on urea, carbonic acid and azote are evolved, and numerous compounds, *alloxan*, *alloxantine*, urea, *parabanic* acid, &c., are formed.

Uric acid is soluble in alkaline carbonates, and in other alkaline salts of feeble acids. Fused with caustic potass it yields carbonate of potass; cyanate of potass, ammonia, &c., being given off. Uric acid may be regarded as carbonic acid, cyanic acid, and prussic acid, $C_{10}N_4$ $H_4O_6$, doubling the equivalent, being equal to $2CO_2 + NC_2O,HO, +$ $3CyH$; uric acid thus representing products of oxidation less advanced than urea. Thus, the formation of uric acid in excess during disease, as in gouty and rheumatic cases, and gravel and calculi, has been attributed to a too copious nourishment, in proportion to the amount of exercise performed by the individual, and to a want of sufficient absorption of oxygen at the lungs, and *defective combustion*. And in support of this it has been remarked, that in reptiles, as serpents, which consume much animal food and are very torpid, the excreta consist almost entirely of lithic acid. Unfortunately for this illustration, the same is the case with birds whose habits are active, and respiration exceedingly energetic, and whose animal heat is higher than that of other animals.

*Urates—salts of uric acid.* It is in the form of alkaline or earthy salts that uric acid principally exists in the body.

*Urate of Soda*, $NaO,C_5HN_2O_2 + HO$, exists normally in the urine of carnivora, in calculi and gravel, in gouty concretions and pulverulent deposits from the urine. Rarely, however, in urinary calculi. It has also been found in the blood in gout. In pulverulent deposits from the urine it exists, as appears by the microscope, in spheroidal or ovoid granules (see fig. 48). The composition of sediments of this nature is to be studied by placing the specimen between two pieces of glass and letting a drop of muriatic acid enter between them. As it enters under, by the microscope, crystals of uric acid will be seen to appear, and will be recognised by their rhomboidal form. *An acid, urate of soda*, containing 2 eqs. of acid to one of base, has also been recognised in the system.

Urate of ammonia exists normally in the urine, and in deposits and calculi. It crystallises in needles often disposed in a fan-like order; it is also found in amorphous deposits.

*The Urate of Lime* is distinguished from the other urates by its solubility, being soluble in 276 of hot, and 603 parts of cold water. It is found chiefly in gouty concretions. When found in deposits it is in little round grains.

*Allantoine*, $C_4H_3N_2O_3$ (Allantoic acid), is obtained from the allantoic fluid of the eow. For this purpose [it is only necessary to evaporate the allantoic fluid to one-fourth of its bulk; the allantoine crystallises on cooling. It is to be purified by boiling with animal chareoal, and repeated crystallisation. It can be made artificially, by boiling uric acid in water, and adding by degrees the peroxide of lead in very fine powder, as long as the pure oxide eeases to lose its eolour; carbonie acid is disengaged, and the filtered liquid deposits allantoine, urea existing in the mother liquid.

Allantoine crystallises in white vitreons prisms. It is tasteless, and without action on the vegetable colours, soluble in 40 parts of hot water, in 160 of cold water. It is soluble in the alkalies, but does not eombine with them; but long boiled with them it is converted into an oxalate with disengagement of ammonia.

*Allanturic acid*, $C_{10}H_7N_4O_9$, is formed in the produetion of allantoine, by the action of nitric acid on allantoine and urea, and also when urea or allantoine is decomposed by the pure colonred oxide of lead; it may be represented as uric acid, $+3HO$.

*Products produced by the action of nitric acid on uric acid.* This is a most extensive series, all connected with uric acid and arising from it principally by the oxidation of some of its elements. The series is too extensive to allow of the description of all its members; they may be resolved according to their formulas, into componnds of carbonic acid, cyanic, prussic, oxalic, formic, alloxanic and sulphurous acids, with cyanogen, carbon, ammonia, and water, taking two, three, or four of these ingredients in their respective compounds.

*Alloxan*, $C_8N_2H_4O_{10}$, (Erythric Acid), is prepared by the action of strong nitric acid on uric acid in the proportion of four of the former to one of the latter. The acid should be added gradually and the vessel kept cool. A crystalline mass is formed which is purified by crystallisation. Alloxan crystallises in rhomboidal prisms. It is extremely soluble in water, has a nauscous and salt astringent taste. It reddens vegetable colours, and hence has been styled an acid. It stains the skin purple. Alkalies convert it in the cold into alloxanie acid; with the aid of heat, into urea and mesoxalic acid. Puce coloured oxide of lead with it produces urea, carbonate, and oxalate of lead. Ammonia in excess changes it into mycomelinic acid: nitric acid produces parabanic acid; muriatic and sulphuric,—alloxan, alloxantine; sulphurous acid and ammonia—thionurate of ammonia; alloxantine and ammonia,—murexide. The chief property of alloxan is its power of forming a solution of a deep blue colonr. when treated with an alkali and a salt of protoxide of iron.

*Alloxanic Acid*, $C_4NHO_4HO$, is another form of alloxan produced by heating alloxan in solution of barytes; a crystalline alloxanate of barytes separates on cooling. It is separable from this salt by the careful addition of $SO_3$ to the barytic salt, and evaporation of the liquid, from which it crystallises. When a solution of alloxanic acid is boiled to dryness, and water then added, a substance called *diffluan* is said to be dissolved, and an aeid named *leucoturic* to remain.

*Mesoxalic Acid*, $C_3O_4,2HO$, is formed when solution of alloxanate of baryta is heated to the boiling point, and then evaporated ; a mixture of urea and mesoxalate of baryta is formed ; this is to be treated with alcohol, which only dissolves the urea ; and mesoxalic acid may be obtained from the salt of baryta by the aid of sulphuric acid. It is a crystalline solid, soluble in water, and not decomposed by boiling. (See preceding sentences.)

*Mycomelic Acid*, $C_8N_4H_5O_5$, is prepared by treating a solution of alloxan with excess of ammonia, and raising the mixture to the boiling point. The solution is then saturated with dilute sulphuric acid, and then boiled for a short time ; on cooling mycomelic acid separates. It is a yellow gelatinous substance soluble in hot, but not in cold water ; it forms salts with the alkalies ; when dried it is a yellow porous powder.

*Parabanic Acid*, $C_6N_2O_4,2HO$ ; is produced when one part of uric acid is treated with eight parts of nitric acid of moderate strength. The liquid is to be evaporated to a syrupy mass, and then left to itself. Colourless scales of parabanic acid separate. It is very soluble in water, and heated with ammonia forms *oxaluric acid*. The *oxalurate of ammonia*, which crystallises out when treated with a mineral acid, yields this new acid as a white crystalline powder.

*Thionuric Acid*, $C_8N_3H_7O_{10}, 2(C_2SO_2)$. A concentrated solution of alloxan is to be treated in the cold with sulphurous acid until the odour of sulphurous acid is perceived. It is then saturated with carbonate of ammonia, and caustic ammonia added. The whole is boiled for a short time, and thionurate of ammonia crystallises on cooling in beautiful colourless plates, which, recrystallised, assume a pink colour. From this salt, by double decomposition with acetate of lead, the thionurate of lead is formed, from which the thionuric acid is separated by sulphuretted hydrogen ; and may be obtained by a careful evaporation. It is a solid, crystallising in needles, of an acid taste ; is very soluble in water, and decomposing, when its solution is boiled, into sulphuric acid and uramile.

*Uramile*, $C_8N_3,H_6O_6$, is formed by treating a concentrated boiling solution of thionurate of ammonia with hydrochloric acid. A white mass is formed in the vessel of a crystalline character. On the whole cooling it is washed on a filter to remove the acid, and dried. The mass is composed of interwoven acicular crystals. It is slightly soluble in hot and insoluble in cold water. Exposed to the air it often becomes pink. It is soluble in the alkalies whence it is precipitated by acids. Boiled along with potass, it is converted into uramilic acid, with disengagement of ammonia. It reduces oxides of mercury and silver forming murexide. Nitric acid converts it into alloxan.

*Uramilic Acid*, $C_{16}N_5H_{10}O_{15}$. Its existence is not well ascertained.

*Aloxantine*, $C_8N_2H_5O_{10}$, may be prepared by boiling a solution of uric acid in 32 parts of water, adding weak nitric acid till the uric acid is dissolved, then evaporating the solution to two-thirds ; the alloxantine is deposited on cooling. It crystallises in four sided oblique rhombic prisms, colourless or slightly yellow, which take a red colour in air charged with ammonia, and acquire a metallic lustre. Alloxantine

reduces the salts of silver. From the action of hydrochloric acid on this substance *alituric* and *dilituric* acids are obtained, likewise *hidantoic* acid.

*Dialuric Acid*, $C_2N_2H_3O_7,HO$, is formed by treating a solution of alloxan or alloxantine with excess of hydrosulphate of ammonia. In this way the dialurate of ammonia is formed, and by decomposing it with muriatic acid, dialuric acid is set free. It is sparingly soluble, and possessed of considerable acid properties.

*Murexide* (Purpurate of Ammonia), $C_{12}N_5H_6O_8$, may be prepared by several processes, by dissolving uric acid in dilute nitric acid, evaporating until the substance assumes a plush red appearance, allowing to cool to 160°, and then treating it with dilute nitric acid, and allowing it to cool, when murexide is deposited; or by boiling together 1 part of uramile with 1 of peroxide of mercury, and 40 of water, with the addition of a little ammonia; as soon as the solution assumes a fine purple colour it is to be filtered, and on its cooling it deposits the murexide. Murexide crystallises in square prisms, which have something of the greenish reflection of the wings of cantharides. Although very little soluble in cold water, it communicates to it some of its fine colour. It is insoluble in alcohol and ether. It is decomposed in boiling water, yielding a yellow deposit. It is soluble in cold solution of potass, which it does not neutralise; but to which it imparts an indigo colour, which disappears on boiling. When dissolved in hot water it gives coloured precipitates with the metallic salts.

*Murexane*, $C_6N_2H_4O_5$ (Purpuric Acid), is prepared by treating murexide by a hot solution of caustic potass, heating the liquid as long as there is any colour, and then saturating with sulphuric acid. On cooling, the murexane separates in colourless or yellowish silky scales, insoluble in water and weak acids. It dissolves in the alkalies and ammonia, assuming a red colour in the latter, especially on exposure to the air, and causing murexide to be formed, which is deposited in crystals. With excess of ammonia it is colourless, and passes into oxalurate of ammonia.

*Xanthic Oxide and Cystic Oxide* are two substances of similar origin to uric acid; they will be treated of under the head of urinary calculi.

*Guanine*, $C_{10}H_5N_5O_2$, is obtained from guano by treating it with muriatic acid, and precipitating the solution by an alkali in the form of a white crystalline powder. There are several other compounds, or alleged compounds, obtainable from uric acid, or the substances derived from it, which have not yet assumed any importance.

# CHAP. V. — SERIES OF THE COMPOUNDS OF THE BENZOLE CLASS, AND ANALOGOUS SERIES.

## SECT. I.—BENZOLE SERIES.

BENZINE, *Bienzole (Bicarburet of Hydrogen, Phene)*, $C_{12}H_6$, is produced when one part of sublimed benzoic acid is distilled with 3 parts of hydrate of lime. The water which condenses in the receiver is surmounted by a fluid colourless liquid which consists of benzine, and which is rectified by a fresh distillation from quicklime. It is produced also when anhydrous benzoates are distilled, but then its formation is accompanied with that of benzone and napthaline. It is also found among the oils condensed from oil gas under a high pressure. When the vapours of benzoic acid are directed upon ignited pumice stone, they are resolved into benzine and carbonic acid: thus $C_{14}H_6O_4 = C_{12}H_6 + 2CO_2$; and thus the production of benzine from the distillation of benzoic acid with lime is accounted for by the fixation of the carbonic acid by the lime as carbonate of lime. Benzine has a peculiar agreeable smell, boils at 186°; at 32° it freezes, and melts again at 44·5°. It is insoluble in water, soluble in alcohol and ether.

*Benzone*, $C_{13}H_5O$ *(Carbobenzine, Carbobenzole)*.—After the distillation of benzine, if the contents of the retort be heated further, the benzoate of lime undergoes a further change, and benzone is distilled over, holding, however, naphthaline in solution, which may be separated by exposing the liquid to a cold approaching zero. It is a pale brown oily liquid, heavier than water.

*Chlorobenzole*, $C_{12}H_6Cl_6$, or $C_{12}H_3Cl_3,3HCl$, is formed when some benzine is exposed in a flask of chlorine to the action of solar light. A thick smoke is formed which condenses on the walls of the flask in transparent white crystals. These are to be washed out with water, in which they are insoluble, and purified by solution and crystallisation in hot alcohol or ether. They melt at 270°, and boil at 550°; and at this temperature, if heated so that it may fall back as condensed into the retort, it yields hydrochloric acid and a substance of the composition $C_{12}H_3Cl_3$, *chlorobenzide, i.e.*, chlorobenzole,—$H_3Cl_3$. This is an oily colourless liquid, which boils at 410°.

Bromine has a similar action on benzine with chlorine.

*Nitrobenzine*, $C_{12}H_5NO_4$ (Nitrobenzide).—Pure nitric acid has little action on benzine; but when fuming nitric acid is used and heated, and the benzine gradually added, the latter gradually dissolves, and on the addition of water, a yellowish liquid is precipitated, which is purified by washing with water, and redistillation. It has a sweet taste and smells like oil of bitter almonds; sp. gr. 1·213°; boils at 415°. In order to explain its formation it is only necessary to withdraw one

atom of hydrogen from benzine by one atom of oxygen of nitric acid, which then becomes $NO_4$ and combines with the $C_{12}H_5$, formed from the benzine.

*Binitrobenzine* is formed by acting upon nitrobenzine by $NO_5$, when another equivalent of hydrogen is withdrawn, and a substance of the formula $C_{12}H_4,2NO_4$ formed. Sulphuric acid acting on benzine forms two compounds, of the formulas $C_{12}H_5SO_2$ and $C_{12}H_62SO_3$, or $C_{12}H_5$ $S_2O_5,HO$.

When nitrobenzine is dissolved in ether, and to the ethereal solution equal volumes of alcohol and diluted hydrochloric or sulphuric acid are added, and some pieces of granulated zinc thrown into the mixture, the nitrobenzine is transformed into a new principle, aniline, which may be displaced by potassa, and removed by agitation with ether. Aniline assumes a purple colour with chloride of lime. The action of the hydrogen disengaged from the zinc and diluted acid is as follows :—

$$C_{12}H_5NO_4 + 6HO = C_{12}H_7N + 4HO.$$
$$\text{Nitrobenzine.} \qquad\qquad \text{Aniline.}$$
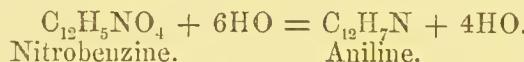
Benzine or Benzole may be viewed as a hydruret of phenyle, $C_{12}H_5H$.

HYDRURET OF BENZOYLE, $C_{14}H_5O_3,HO$ (Essential Oil of Bitter Almonds).—The leaves of the cherry laurel, or the kernels of bitter almonds, distilled along with water, furnish a volatile oil which is a complex mixture, of which the chief ingredient is the hydruret of benzoyle; it contains also benzoic acid, prussic acid, benzone, &c. The kernels of bitter almonds are generally used, and freed from fatty oil by pressure. The expressed kernels are then mixed with water, and after standing some time distilled. To purify the hydruret of benzoyle, it is best mixed with water, perchloride of iron, and slaked lime, so as to form a thickish mass, which is to be distilled, and the product redistilled from chloride of calcium. In commerce, the first product is redistilled with common salt; prussic acid must be separated from this product by distillation over red oxide of mercury, and the whole distilled from unslaked lime. No essential oil exists in the cells of the kernels, but there exist two substances, amygdaline and emulsine, which are prevented from acting on each other by the presence of fat. As soon as this is removed, and the two substances in contact with water, then they act on each other, and the oil is formed. The hydruret of benzoyle is liquid, colourless, and transparent, very refrigerating. It has a burning taste, and a pungent smell, like that of prussic acid; sp. gr. $1\cdot044$, boils at $356^\circ$; passed in vapour on hot pumice-stone; it is resolved into carbonic acid and benzine; and it burns in air with a white smoky flame. Exposed to the air it absorbs atoms of oxygen, and is converted into benzoic acid.

BENZILE OR BENZOYLE, $C_{14}H_5O_2$ or $C_{28}H_{10}O_4$.—The supposed radical of the benzoyle series has been obtained; but like many other bodies corresponding in composition to these supposed radicals, when obtained

its quality of radical has become doubtful. It is formed by passing chlorine into fused benzoine as long as muriatic gas is envolved. The product which results is dissolved in boiling alcohol, and the benzile crystallises from the solution in transparent yellow prismatic crystals. It melts at 197—8°, insoluble in water, but soluble in ether as well as alcohol.

BENZOYLE OR BENZYLE, Bz, $C_{14}H_5O_2$, supposed to be the true radical of the benzoyle series is obtained from the dry distillation of the benzoate of copper. The products contain benzoic and salicylic acids, and an oil which crystallises on cooling. It fuses at 158°, and as when heated with hydrate of potassa, benzoic acid is formed with evolution of hydrogen, it is supposed to be the radical of benzoic acid, which is the oxide of it.

BENZOIC ACID, $C_{14}H_5O_3,HO$, or $BzO,HO$.—It may be obtained by an elegant process by distillation from gum benzoine. The gum, powdered with sand, is placed in a shallow iron-vessel, and over it is secured a piece of filtering paper, while an ordinary paper cap is tied over this. The vessel is then heated gradually by a sand-bath. The oil of the gum is retained by the filtering paper, through which the vapour of benzoic acid passes, and is condensed on the outside or in the paper cover. The most usual way, however, is to boil the gum benzoine with slaked lime or carbonate of soda. When slaked lime is used 8 parts of the gum powdered should be mixed with 3 or 4 parts of slaked lime, then powdered with a little water, and boiled with 80 parts of water. In this way a solution of benzoate of lime or soda is obtained, which is concentrated to one-fifth and decomposed by hydrochloric acid, when benzoic acid is separated in crystals, which must be purified by crystallisation. By the former process the acid is obtained in light feathery hexagonal crystals; by the latter in transparent flexible crystalline plates. When perfectly pure, benzoic acid is inodorous. The odour which it sometimes possesses is due to the presence of an oil which accompanies it. It has a sweetish taste, and creates a peculiar sensation at the posterior fauces. It reddens litmus, melts at 249°, and boils at 462°; but begins to sublime at 293°. It burns in contact with air. It is soluble in 200 parts of cold and 25 of boiling water; it dissolves in 2 parts of alcohol, is very soluble in ether and in fixed and volatile oils. The benzoates are formed by the substitution of 1 eq. of base for one of water. They resemble closely the cinnamates, from which they are distinguished in not producing essence of bitter almond when boiled with sulphuric acid and bichromate of potass. The alkaline benzoates are soluble, and crystallise with difficulty. The benzoates of baryta and strontia are insoluble in cold but soluble in boiling water. The benzoate of lime is soluble in 20 parts of cold and very soluble in boiling water. The benzoate of ammonia is a crystallisable deliquescent salt, which is converted by dry distillation into a substance of the formula $C_{14}H_5N$, benzonitrile, which also is produced with other substances. This is a yellow oil, smelling like oil of bitter almonds. It sinks in water, is soluble in alcohol and ether, and boils at 374°. It may be regarded

as benzoate of ammonia, less 4 eqts. of water, or $NH_4O,C_{14}H_5O_3$—$4HO$ $=C_{14}H_5N$. Benzoate of ammonia may be employed to precipitate peroxide of iron from acid solutions, but the muriate is preferred.

*Benzoine*, $C_{14}H_6O_2$ or $C_{28}H_{14}O_4$, is an isomeric modification of bitter almond oil. It exists ready formed in the crude essence of bitter almond oil. In order to obtain it, lime or barytic water must be added to this; and the mixture kept for some time at the temperature of 177°, furnishes benzoine on cooling : or it may be obtained by mixing the pure essence with potass, dissolving it in alcohol, and adding prussic acid to the mixture. It crystallises in brilliant transparent prisms, without taste or smell. It fuses at 248° into a colourless liquid, which crystallises on cooling. It is volatile without change. Its vapour is very inflammable; passed through a red-hot tube, it reproduces the hydruret of benzoyle. It is insoluble in cold water; and slightly soluble in hot water, from which it crystallises in fine needles. It is less soluble in hot than in cold alcohol. It communicates to sulphuric acid a violet colour, and on heat being applied, $SO_2$ is liberated. Fused with potassa, it forms benzoate of potass.

*Benzilic Acid*, $C_{28}H_{11}O_5HO$, is formed by dissolving benzyle or benzoine in a boiling alcoholic solution of potassa. At first the solution has a violet tint; the boiling is continued until the solution becomes colourless. The solution of benzilite of potass which is formed, is then filtered and decomposed by muriatic acid. On cooling, small transparent rhombohedral crystals, of the composition above indicated, are deposited, or sometimes long prismatic needles. It is soluble in boiling water, but very slightly so in cold water; soluble in alcohol and ether. Concentrated sulphuric acid decomposes it, and produces a fine violet colour; the colour remains for some time, and then disappears on the addition of water. It forms alkaline and other benzilites. It may be regarded as a compound of 2 eq. of benzyle and 1 of water.

Chloride of Benzoyle, $C_{14}H_5O_2Cl$, is prepared by the action of dry chlorine gas on bitter almond oil. The gas must be passed through the oil as long as hydrochloric acid is disengaged ; the liquid, which is yellow, is then to be heated until it becomes colourless. A colourless liquid is thus obtained of a strong disagreeable odour, which irritates the eyes; has a sp. gr. 1·106, and boils at 383°, and burns with a smoky flame, bordered with green. It may be distilled from anhydrous chalk or baryta, without alteration ; when thrown into water it is gradually decomposed into benzoic and hydrochloric acids, according to the following formula:—

$$C_{14}H_5ClO_2 + 2HO = C_{14}H_6O_4 + ClH.$$

Chloride of benzoyle.      Benzoic acid.
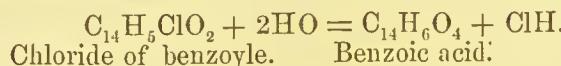
On the same principle with an alkali in solution, it yields a benzoate and a chloride.

A bromide, an iodide, a sulphuret, and a cyanuret of benzoyle can also be formed.

## COMPOUNDS OF BENZOIC ACID WITH OTHER ACIDS.

*Nitrobenzoic Acid*, $C_{14}H_5(NO_4)O_4$.—Nitric acid, in large excess, dissolves benzoic acid, assuming a red colour, and disengaging nitrous fumes. After a time these cease, and the liquid becomes colourless; and, on cooling, crystals of the new acid are deposited and purified by repeated crystallisation. This acid is soluble in boiling water. The crystals fuse in water below the boiling point; but, when dry, they require a higher temperature. They sublime at 230° without decomposition. They are soluble in alcohol and ether. The nitrobenzoates explode when strongly heated; by a moderate heat, they give rise to nitrobenzoine. The nitrobenzoate of silver is especially explosive. Another acid may be formed from benzoic acid by the joint action of nitric and sulphuric acid, termed the binitrobenzoic, $C_{14}H_4,2(NO_4),O_4$.

*Sulphobenzoic Acid*, $C_{14}H_4O_3,S_2O_5,2HO$, has been obtained by directing the vapours of anhydrous sulphuric acid into a dry and cool receiver containing benzoic acid. A viscous mass is formed, which is dissolved in water and neutralised by carbonate of baryta. The solution is concentrated, filtered, and decomposed by hydrochloric acid. Sulphobenzoate of baryta crystallises on cooling. This salt is soluble in 20 parts of cold water. It is dissolved and decomposed by sulphuric acid; the solution concentrated by heat, and finally in vacuo over sulphuric acid. Sulphobenzoic acid forms colourless deliquescent acid crystals, which are very permanent. The sulphobenzoates are generally soluble and crystallisable.

*Formobenzoic Acid*, $C_{14}H_6O_2+C_2HO_3,HO$ (formobenzoilic acid), is obtained by dissolving crude almond oil in dilute muriatic acid, and evaporating to dryness, and dissolving the residue in hot ether. The formobenzoic acid is dissolved, and a residuum of muriate of ammonia remains. The etherial solution leaves crystals of the acid. They are decomposed by heat, evolving a peculiar smell like the hawthorn blossom, and leaving a carbonaceous residue. When the watery solution of formobenzoic acid is heated with chlorine, nitric acid, or peroxide of manganese and sulphuric acid, it is resolved into carbonic acid and essence of bitter almond. Its salts are definite and crystallisable, and in which 1 eq. of water in the acid is replaced by 1 of base.

These acid compounds of benzoic acid, the formobenzoic acid, and benzoic acid itself, form ethers.

### OTHER COMPOUNDS OF THIS CLASS HAVING MORE DIRECT RELATIONS WITH AMMONIA.

*Benzamide*, $C_{14}H_5O_2,NH_2$, is obtained by the reaction of dry ammoniacal gas on the chloride of benzoyle. A solid white mass is produced, which is to be powdered and washed with cold water to remove the sal-ammoniac which is formed at the same time, and which is then to be dissolved in boiling water, whence the benzamide crystallises on cooling. It may be obtained by other processes.

It is colourless and transparent; crystallises in right rhomboidal prisms, or in pearly tables. It melts at 237°, and is volatilised at a higher temperature. It is soluble in alcohol and ether. Benzamide is soluble in bromine; and, after some time, and under the influence of cold, red ruby crystals are deposited of bibromide of benzamide, $C_{14}NH_7O_2,Br_2$.

*Hydrobenzamide,* $C_{42}H_{18}N_2$, is obtained by digesting 1 volume of bitter almond oil, and 20 volumes of strong liquid ammonia, at a temperature of from 104° to 120°. The vessel being closed, is found, after some hours, to be filled with a mass of crystals, which are to be washed with cold ether, which leaves the hydrobenzamide undissolved. This is to be dissolved in cold alcohol, which yields it in regular crystals by spontaneous evaporation. These are octahedral or rhomboidal prisms, without colour, inodorous, and insipid; melt at 230°, and are decomposed by dry distillation, yielding a carbonaceous residue. It is insoluble in water. Its formation is explicable when we consider the reaction of three equivalents of hydruret of benzoyle on two of ammonia. $3(C_{14}H_6O_2)+2NH_3=C_{42}H_{18}N_2+6HO$. The alcoholic solution, when boiled, reproduces ammonia and hydruret of benzoyle. Under the action of reagents many substances are formed from it, especially *amarine,* or *benzoline,* termed also *picromine.*

*Benzimide,* $C_{28}H_{11}NO_4$, is found in the residue of the distillation of oil of bitter almonds, exhausted by boiling alcohol, from which it crystallises in needles or flocculi.

Numerous other compounds of this series exist—too numerous for further description;—for instance, a group of bodies which have been designated as compounds of benzoinene, or stilbene. Stilbene is supposed to be derived by the augmentation of benzine by a certain number of eqts. of carbon. $2(C_{12}H_6)+4C=C_{24}H_{12}C_4$, benzoinene. Benzoinene itself is obtained by dissolving one volume of the crude essence of bitter almonds in ten or twelve of alcohol, and then adding, by degrees, a volume of hydrosulphate of ammonia. The liquid becomes troubled at the end of a few minutes, and deposits a powder similar to flour. The alcoholic solution should be carried to the boiling point. The white precipitate is to be washed with boiling alcohol. From this substance the benzoinene is obtained by distillation.

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## SECT. II.—HIPPURIC ACID, $C_{18}H_8NO_5,HO$.

The best mode of obtaining this acid appears to be to evaporate the fresh urine of the horse or cow, and especially that passed in the morning, to one-eighth of its bulk, to precipitate in the cold by hydrochloric acid, and to express strongly the precipitate, which is to be put into about ten times its bulk of boiling water, with an excess of milk of lime; then filtering, expressing the residue, and filtering and adding alum to the solution till it ceases to be alkaline. Then it is to be

raised to the temperature of 104°, and bicarbonate of soda added till a precipitate ceases to be formed. Filtration is again repeated, the precipitate again expressed, and the clear liquid treated by muriatic acid. Finally, the hippuric acid thrown down is dissolved in boiling water, decolorised by animal charcoal, and separated by the addition of muriatic acid to the hot filtered solution. It crystallises ordinarily in long semi-transparent square prisms, terminated by dihedral summits. The crystals are colourless, or slightly yellow, have a bitter taste, and redden litmus strongly. They melt on being heated, and form an oily liquid. They are soluble in about 400 parts of water at 60°, and extremely so in boiling water and alcohol, less so in ether. On being strongly heated in a tube, drops are formed, and on cooling, a black matter is found at the bottom of the tube, and the sides are encrusted with a crystalline efflorescence of benzoic acid and the benzoate of ammonia. On pushing the heat further, prussic acid is disengaged, and a carbonaceous residue remains.

The theoretical composition of hippuric acid admits of several constructions. It is most probably and simply regarded as containing the elements of benzoic acid and sugar of gelatine, minus water. Thus:—

$$C_{14}H_5O_3HO + C_4H_4NO_3HO = C_{18}H_8NO_5HO + 2HO.$$
Benzoic acid. Sugar of gelatine. Hippuric acid.
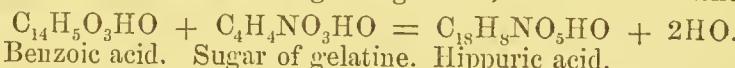
And the simple ebullition of the solution of hippuric acid in presence of the mineral acids is sufficient to accomplish this decomposition.

Hippuric acid is distinguished from benzoic acid by the form of its crystals. It exists in small quantity, normally in the urine of man, and in larger quantity in disease ; some of its crystals obtained from urine are shown in fig. 49. Where hippuric ether exists free, it may be extracted by agitating the fluid containing it with ether in a flask, when the hippuric acid crystallises on spontaneous evaporation. It may be obtained from human urine by evaporating this fluid to a syrup, by means of a water-bath, adding a little hydrochloric acid, then agitating the extract with its volume of ether. This removes the hippuric acid, and forms an upper layer, to which, at the end of an hour, about 1-20th of alcohol is added. The upper layer is decanted, agitated with small portions of water, which dissolve the urea and alcohol, while the hippuric acid remains in the ether, and separates by spontaneous evaporation in crystals.

When benzoic acid is administered internally, it appears in the urine in the form of hippuric acid. *Hippurates* exist in the system in the form of hippurates of soda, lime, and ammonia.

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SECT. III.—NAPHTHALINE, $C_{10}H_4$, OR $C_{20}H_8$, AND ITS PRODUCTS.

Naphthaline is formed during many processes in the preparation of soot, in the rapid decomposition of bicarburet of hydrogen by chlorine, the distillation of white pitch and camphor, and in all probability in

all cases where the decomposition of organic substances takes place at a high temperature, and if the empyreumatic products of such distillation are redistilled at a high temperature, the quantity of naphthaline increases.    It is found in larger quantity in coal tar than in wood tar, and the quantity is increased by the age of the tar.    The best mode of preparing it is to distil coal tar, then to collect the oil distilled and pass a current of chlorine into it for four days.    Hydrochloric acid is disengaged, and the oil becomes black.    It is then washed with water, which extracts hydrochloric acid, and an indeterminate substance.    It is then distilled until a porous carbon is left, and the product of the distillation cooled to 14° yields a deposit of naphthaline, which is purified by repeated crystallisation from alcohol.    It crystallises for the most part in rhomboidal plates.    Its sp. gr. is 1·048; it melts at 176°, boils at 414°.    It has a rather agreeable smell; is somewhat soluble in boiling water, in four parts of boiling alcohol, and very much so in ether and fat and essential oils.    A mixture of equal parts of axunge and naphthaline exposed to the air blackens, absorbing oxygen and giving off carbonic acid.    After some weeks, when the mass is exhausted by ether, an insoluble part is found, which, however, is soluble and crystallisable from alcohol.    Chlorine has extensive re-actions upon naphthaline, removing equivalents of hydrogen, and sub-stituting chlorine.    In this way a series of compounds is formed from the protochloride, $C_{20}H_7Cl$, to the perchloride, $C_{20}Cl_8$.    Bromine has a similar action; and as these compounds combine with each other a prodigious number of compounds may be formed.

Naphthaline dissolves in sulphuric acid with the aid of a gentle heat, and forms a red-coloured solution, which, saturated with baryta, yields several acid compounds.    Nitric acid acts on naphthaline in a manner, in some respects, similar to chlorine, successively eliminating an atom of hydrogen, and replacing it by an atom of $NO_4$.    The *protonitrate* of naphthaline is formed by boiling naphthaline with nitric acid. An oil is quickly formed, which solidifies on cooling.    By crystallising this from alcohol, a pure protonitrate of naphthaline is obtained.    It is a yellow substance like sulphur, insoluble in water, and very soluble in hot alcohol, ether, and chloride of sulphur.    It is deposited from these solvents in friable, needle-like prisms.    When distilled from baryta, besides other products, a solid, termed *naphthase*, of the formula $C_{20}H_7O$, is formed.    Napthalidame, or naphthalidine, $C_{20}H_9N$, is a product of the reaction of sulphuretted hydrogen and alcoholic solution of pro-tonitrate of naphthaline, to be spoken of immediately.

Sulphuric acid dissolves naphthaline readily, the syrupy solution heated to 194°, and abandoned to the air, absorbs moisture, becomes violet, and solidifies.    This mass, on a dried tile, under a bell glass, separates, and solid scaly plates separate, soluble in water and alcohol. This is a mixture of two acids which, saturated by carbonate of lead, form two salts, both equally soluble in water, but differently soluble in alcohol.    One of the salts, the sulphonaphthalic, being soluble in boiling alcohol, the other, not so soluble, is termed sulphonaphthic.    Their formulas are respectively $C_{20}H_8,2SO_3,HO$, and $C_{20}H_7S_2O_5,HO, + Aq.$

Several other acid and neutral compounds are formed by the action of $SO_3$ on naphthaline.

*Phthalic* or naphthalic acid, $C_{16}H_6O_8$, or $C_{16}H_4O_6,2HO$, is prepared by treating the perchloride of naphthaline, $C_{20}H_8Cl_4$, by nitric acid at the boiling point, and heating until the greater part of the nitric acid is distilled. In the retort there remains a crystalline mass, which, washed with cold water and distilled several times in boiling water, yields yellowish white plates, which collect in rounded groups. This is naphthalic acid, slightly soluble in cold water, very soluble in alcohol and ether. It forms a class of salts. When the acid, phthalate of ammonia is distilled, a substance sublimes in light scales, which has the composition $C_{16}H_4O_4,NH$—and is called *pthalimide*.

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### SECT. IV.—COMPLEX SUBSTANCES OF THE BENZOIC SERIES.

*Athamantine,* $C_{24}H_{15}O_7,HO$, is a fatty crystalline substance found in the root of the athamanta oreoselinum. It is obtained from the root by extraction with alcohol, and then acting on the dried alcoholic extract with ether. It crystallises in long needles. When boiled in hydrochloric acid, it is separated into *oreoseline*, which dissolves, and valerianic acid, which is driven off. The formula of the former is the same as that of hydrated benzoic acid, $C_{14}H_6O_4$, and added to that of valerianic acid, $C_{10}H_{10}O_4$, makes up athamantine. From the solution in water, oreoseline may be separated by crystallisation with the application of cold. It melts when heated, and then is decomposed; soluble in alcohol and ether. It has been considered the glycerine of athamantine.

*Amygdaline* $C_{40}H_{27}NO_{22}$. This substance may be regarded as a compound of prussic acid, hydruret of benzoyle, grape sugar, and formic acid, all which principles can be obtained from amygdaline. Thus :—

| | | |
|---|---|---|
| Prussic acid . . . . | $C_2NH$ | |
| Hydruret of benzoyle . | $2(C_{14}H_6O_2)$ | |
| Grape sugar . . . . | $C_6HO_7$ | $C_{40}H_{21}NO_{22}$ |
| Formic acid . . . . | $2(C_2HO_3,HO)$ | |
| Water . . . . . . | $3HO$ | |

The kernels of bitter almonds are composed of cellular tissues, and include in their cells, besides amygdaline, which exists in the proportion of three or four per cent., sugar, gum, albumen, and a particular azotised matter, emulsine. The amygdaline is separated by the following process. The almonds are first pressed between two plates of hot iron to express the oily matter. The residue is then treated with boiling alcohol of 93 or 94 per cent., in successive portions. The extract is evaporated over the water bath till it assumes a syrupy aspect. It is then diluted with water, and left, with the addition of yeast, in a hot place. The object is to get rid of the sugar by fermentation.

When the fermentation has ceased it is again evaporated over the water bath to the consistence of a syrup. The syrup is exhausted with alcohol of the same strength as before, which deposits the amygdaline as a white crystalline powder, which is to be purified by repeated crystallisation from alcohol. The crystals are scales from alcohol,—fine prisms when from water. It is very soluble in alcohol and water, and insoluble in ether. Its watery solution is bitter. It is inodorous except when heated. It then smells, diffuses the odour of hawthorn blossoms, and yields, when distilled, an ammoniacal product. When distilled with weak nitric acid, or with a mixture of peroxide of manganese and sulphuric acid, it yields ammonia, benzoic acid, hydruret of benzoyle, formic and carbonic acids. By solutions of the caustic alkalies, it is transformed into amygdalic acid, ammonia being evolved.

*Amygdalic acid*, $C_{40}NH_{26}O_{24},HO$, is a soft crystalline mass, which may be obtained by decomposing the amygdalate of barytes formed as just described, with sulphuric acid. It may be regarded as a compound of oil of bitter almonds, anhydrous formic acid, and sugar.

*Emulsine or Amandine, Synaptase.* This substance, about whose precise nature there is some doubt, may be described as an albuminous principle residing in the sweet and bitter almond, having the same kind of relation to amygdaline that diastase has to starch, as has already been described under the head of oil of bitter almond. The process formerly given for preparing it was, to diffuse through three parts of distilled water one part of flour of sweet almonds from which the oil has been expressed, and to leave this for five or six days at a temperature of from 68° to 77°, in a vessel not quite closed. The fermentation produces a thick layer of coagulate of albumen at the top, which is to be removed; and the emulsine remains in solution in the liquid, which is to be quickly filtered. This liquid, which is acid, is mixed with its own bulk of alcohol of 82 per cent, and the white precipitate formed, washed with alcohol and dried at 96°. It is to be freed from salts by digestion in water, filtration, and a fresh precipitation with alcohol. Thus prepared it is a horny gummy mass, tasteless and inodorous, soluble in water, slightly acid, insoluble in alcohol and ether. The precise nature of the albuminous compounds found in sweet and bitter almonds has been rendered doubtful by recent researches. The substance thus described has the properties ascribed above; its formula has been given $C_{20}H_{25}N_2O_{32}$.

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### SECTION V.—SALICYLIC SERIES.

The relations of this class have reference to a formula which may be considered as that of benzene plus 2 of oxygen, or $C_{12}H_6O_2$. Their analogy with the compounds of the benzoic class may be shewn theoretically and practically. Thus the benzoate of copper, in distillation, is converted into salicylic acid by absorbing two equivalents of oxygen, thus :—

$C_{14}H_5O_2O,HO$ benzoic acid, or hydrate of the oxide of benzoyle, $+2O = C_{14}H_5O_4O,HO$, salicylic acid, hydrate of the oxide of salicyle. Again, a compound analogous to the oil of bitter almonds of the salicylic class is the oil of *spiraea ulmaria*, and as the hydruret of benzoyle is $C_{14}H_5O_2,H$, so is that of salicyle (the volatile oil in question), $C_{14}H_5O_4,H$. The substance, however, actually corresponding to benzene, with this addition of two equivalents of oxygen, is phenole, or carbolic acid. The compounds of the salicylic acid group offer many examples, even by their very varied terminology, of the different ideas entertained by chemists of the actual mode in which these series should be classed. Here, as elsewhere in this work, the object is to range them as practically as possibly, without committing, as far as possible, the fault of confining the ideas of the student to what may be the mere theory of the day.

SALICINE, $C_{26}H_{18}O_{14}$, may be regarded as phenole (carbolic acid), and grape sugar, $C_{12}H_6O_2 + C_{12}H_{12}O_{12}$, or saliretine, which has the same composition as phenole, with the same.

Salicine is prepared by exhausting willow bark with boiling water, concentrating the decoction, and adding litharge to it until it is colourless, saturating in part the oxide of lead by sulphuric acid, and precipitating both the sulphuric acid, if any should be in excess, as well as the lead, by sulphuret of barium, which must be carefully added so as not to be in excess, then evaporating and recrystallising, using animal charcoal, if necessary, to purify the salicine ; or, more simply, by precipitating the decoction of willow bark by sugar of lead, diffusing the precipitate in water, decomposing it by sulphuretted hydrogen, filtering, evaporating, and crystallising the salicine, using animal charcoal if requisite.

Salicine crystallises in needles or in white plates, which are inodorous, bitter, and without effect on vegetable colours ; they are not affected at 212° ; melt at 244°, and are coloured and decompose at a higher temperature. They are soluble in 20 times their weight of cold water, and extremely soluble in hot water; soluble in alcohol, but insoluble in ether, fat oils, and turpentine ; not precipitated by subacetate of lead, tannine, or gelatine. Sulphuric acid dissolves salicine in the cold, and assumes a deep red colour ; and this test enables salicine to be detected in willow bark.

Weak sulphuric and muriatic acids decompose by boiling salicine into grape sugar and saliretine, $C_{26}H_{18}O_{14} + 2HO = C_{14}H_6O_2$ (saliretine) $+ C_{12}H_{14}O_{14}$, the saliretine being isomeric with the essence of bitter almonds. Chromic acid converts salicine into formic acid and the hydruret of salicyle.

The ordinary ferments have no action on salicine, but emulsine or synaptase, which possesses the power of acting as a ferment or catalytic agent on amygdaline, and producing from it the oil of bitter almonds, has also the property of acting upon salicine in a similar way, and resolving it into grape sugar and saligenine, $C_{26}H_{18}O_{14} + 4HO = C_{14}H_8O_4$ (saligenine) $+ C_{12}H_{14}O_{14}$.

*Saligenine*, $O_{14}H_8O_4$, or $C_{14}H_6O_2,2HO$, is prepared by bruising 50 parts

of well powdered salicine in 200 parts of distilled water, and adding three parts of emulsine to the mixture; the whole is to be introduced into a flask, well agitated and heated in the water bath to 104°. In 10 or 12 hours the change is effected, and the saligenine crystallises in groups of rhombohedral crystals. The remaining liquid, agitated with successive portions of ether, yields further crops of crystals on the evaporation of ethereal solutions, which are to be purified by solution in boiling water and recrystallisation. The grape sugar produced at the same time can be subjected (as a test) to fermentation. Saligenine is in brilliant pearly crystals. It is soluble in 15 parts of water at 72°, and in all proportions in boiling water; very soluble in alcohol and ether, melts at 180°, is volatile at 212°, and is converted by the prolonged action of heat into saliretine, producing at the same time some water and hydruret of salicyle. Weak acids change it into saliretine.

*Saliretine,* $C_{14}H_6O_2$.—This body, whose modes of formation have been already indicated, is deposited from aqueous solutions of salicine boiled with weak sulphuric or hydrochloric acids, as a white or yellow resinoid substance.

HYDRURET OF SALICYLE, $C_{14}H_6O_4$, or $C_{14}H_5O_4.H$ (Salicylous Acid, Hydruret of Spirole).—The imaginary radical silicyle has the formula, $C_{14}H_5O_4$. If it be the base of the salicylic compounds, then this substance is its hydruret, as bitter almond oil is the hydruret of the radical benzoyle.

The hydruret of salicyle may be prepared artificially from salicine, or from the spiraea ulmaria (meadow sweet). When prepared in the former way, the following proportions are employed :—3 parts of salicine, 3 of bichromate of potass, 4·5 of concentrated sulphuric acid, and 36 of water. The bichromate is mixed with the salicine, and then two-thirds of the water are added, and the whole shaken in the retort; then all the sulphuric acid diluted with another third of the water is added, and the agitation repeated. The reaction is established by degrees, but is soon calmed; heat is then moderately applied, and the product distilled carefully condensed. It is a watery acid liquid, containing formic acid, and is oily, of a red colour, at the bottom of the watery portion. This is the almost pure hydruret of salicyle, which is to be digested for twenty-four hours over chloride of calcium, decanted and distilled. The oil of spiraca does not exist ready formed in the flowers of the plant, which can be exhausted by alcohol without a trace being found in the extract of the hydruret of salicyle; but it is formed when these flowers are distilled in contact with water, and a fluid is thus obtained, containing the hydruret of salicyle along with substances analogous to turpentine and camphor. When this fluid is mixed with potass, the hydruret of salicyle combines with the potass, and remains fixed, while the other substances can be separated by distillation : the hydruret is set at liberty by the addition of sulphurous acid and distillation.

Hydruret of salicyle is a colourless liquid, reddening in contact with air, and with a smell very similar to that of bitter almonds. It has a

hot and burning taste, and forms on the skin yellow spots, somewhat like those produced by iodine; sp. gr. 1·173, boils at 385°. It is very soluble in water, and in all proportions in alcohol and ether. Although it does not redden litmus, it decomposes the alkaline carbonates in the cold. It colours the persalts of iron of a deep violet. When heated with potass, hydrogen is disengaged and salicylic acid formed. With the alkalies and bases it forms salicylites; several other compounds with chlorine, &c. Ammoniacal gas is absorbed by the hydruret of salicyle, and a yellow crystalline compound formed; but if the salicylous acid be dissolved in three volumes of alcohol, and the caustic ammonia be added, drop by drop, a mass of yellow needles is formed. This substance has been called *salicylimide*, and has the formula $C_{42}H_{18}N_2O_6$.

*Salicylic Acid*, $C_{14}H_6O_6$, may be regarded as a compound of $C_{12}H_6O_2$, which represents, or may represent, the formulas of so many substances, and $2CO_2$. It is prepared by heating the hydruret of salicyle with an excess of hydrate of potass as long as hydrogen is disengaged, dissolving the mass in water, and throwing down the salicylic acid formed by muriatic acid. It is then to be dissolved and crystallised several times by means of boiling water.

This acid is soluble in hot water, from which it crystallises on cooling, very soluble in alcohol and ether. It volatilises and crystallises on sublimation almost like benzoic acid. It reddens litmus, and decomposes carbonates. Its watery solution assumes the colour of ink when persalts of iron are added to it.

*Nitrosalicylic Acid*, $C_{14}H_4NO_9HO$, was obtained at first by the action of nitric acid on indigo, and hence termed indigotic acid and anilic acid. In this way it is obtained by adding indigo, in small quantities at a time, to a mixture of 1 part of nitric acid and 10 or 12 parts of water, at the boiling point. The nitrosalicylic acid is deposited on cooling, and may be purified by repeated crystallisations. It may also be produced by the direct action of fuming nitric acid on salicylic acid. The result is a resinoid mass, which is to be washed with cold water, and dissolved in boiling water, whence the nitrosalicylic acid crystallises in the form of yellow needles, which are fusible and volatile. In the process from indigo the indigotic acid may be obtained in solution in boiling water, precipitated by acetate of lead in the form of anilate of lead, and the acid separated by sulphuric acid.

*Methylosalicylic Ether*, $C_{14}H_5O_5,C_2H_3O$.—This ether is remarkable as existing ready formed in the winter green *gualtheria procumbens*. The oil of this plant can be extracted directly from the flowers by means of alcohol and ether. The crude oil is yellow, with a strong, sweet, and persistent odour. The ether is separated from the oil by distillation, when the temperature rises to 432°; below that, other substances distil over. It is a colourless liquid, having the odour of the crude oil, sp. gr. 1·18, very soluble in alcohol and ether, slightly so in water.

### SECT. VI.—PHENIC COMPOUNDS.

This series possess the relation to the formula $C_{12}H_6O_2$ so remarkable in the benzoic and salicylic series, but like them they exhibit many irregularities of composition. The compound radical of this series is assumed to be phenyle, $C_{12}H_5$, sym. Pyl., of which carbolic acid is the hydrated oxide, isomorphous with the oil of bitter almonds.

*Carbolic Acid*, $C_{12}H_6O_2$, or $C_{12}H_5O,HO$, is termed also phenic acid and phenole. It is very similar to creasote, and is found among the products of the distillation of tar. To prepare it, those portions of the oils must be collected which distil between 300° and 400°. Into these a hot saturated solution of potass is poured, as well as potass in powder. The oil becomes a crystalline mass, and a disagreeable odour is disengaged. The liquid parts are decanted; and the solid dissolved in hot water. Two layers then form, one light and oily, which is to be removed; the other, heavy and watery, which is to be treated with hydrochloric acid. From this arises an oil which is to be digested with chloride of calcium and distilled several times. An oily liquid is thus obtained, a little heavier than water, whose boiling point is 368°, and which solidifies when the receiver is cooled.

It is a white crystalline solid which melts at 93°, and liquefies under many indeterminate circumstances; a little humidity, for instance, will produce this effect. It burns with a smoky flame. Sulphur and iodine are soluble in it without change. Chlorine, bromine, and nitric acid act powerfully upon it. Carbolic acid is of somewhat doubtful acid properties. It does not combine with ammonia, or redden litmus, and dissolves carbonate of potass without displacing carbonic acid. It absorbs ammonia, and if then heated between 400° and 572°, in a hermetically sealed tube, it forms, after several days, aniline, $C_{12}H_6O_2$ $+NH_3=C_{12}H_7N$(aniline)$+2HO$.

Carbolic acid is a corrosive substance, coagulating albumen, and acting upon the mucous membranes,—like creasote it arrests putrefaction. A slip of deal, immersed in a solution of carbolic acid, and then in nitric acid, becomes bluish brown. It is slightly soluble in water; in all proportions in alcohol, ether, and acetic acid.

Chlorine forms several compounds with it, as does bromine. Nitric acid also combines with it in several proportions. The most important of these compounds is the trinitrophenic, carbazotic, or picric acid.

*Picric acid*, $C_{12}H_3,3NO_4O_2$. The substances long known to produce this acid were generally azotised and of animal origin, as fibrine, silk, aloes; afterwards it was found to be derivable from a great many substances, indigo, salicine, benzoine, aloes, coumarine, &c. To prepare it, one part of bruised indigo is to be treated at a moderate heat with eight or ten parts of nitric acid. After considerable effervescence, the liquor is to be brought to the boiling point, and more nitric acid added as long as red fumes are disengaged. On cooling, the picric acid crystallises in brilliant yellow crystals. When the

mother liquid is diluted with water it yields a brownish mass, which treated with boiling water affords a new mass of crystals of picric acid. This is to be purified by solution in hot water, saturation by carbonate of potass, and decomposition of the alkaline picrate formed by a strong acid. It is more economically prepared from oil of tar or salicine. It crystallises in rectangular plates, or yellow six-sided prisms. It is soluble in alcohol and ether, has an acid and bitter taste, melts by a gentle heat and is partially volatilised, detonates when strongly heated. It has a bitter taste, and reddens litmus.

*Styphnic Acid*, (oxypicric), $C_{12}N_3H_3O_{16}$, is obtained by treating assafœtida, several gums, resins, or Brazil wood, with nitric acid. It forms yellow seven-sided prismatic crystals, and very much resembles the preceding compound.

*Helicine*, $C_{26}H_{16}O_{14}$, is prepared by acting on salicine with 10 eqts. of nitric acid, sp. gr. 1·16.

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## SECT. VII.—INDIGO AND ITS DERIVATIVES.

*Indigo Blue*, $C_{14}H_5NO_2$, is isomeric with the cyanide of benzoyle, so that it might have been classed with the benzoic series; but the products of oxidation of indigo are so numerous as to connect a whole series of substances with indigo blue, of which isatine is the principal term. These products differ from indigo blue, chiefly by the addition of 2 eqts. of oxygen; that is to say, the isatic compounds have the same relation to indigo blue that the salicylic series have to the benzoic. Isatine especially has the formula of cyanide of salicyle. Whether or not these products are true cyanides, the group of indigo blue compounds differ from that of the hydruret of benzoyle, solely by the substitution of the bicarburet of azote for an equivalent of hydrogen; and isatine is in the same relation to the hydruret of salicyle. The products derived from indigo have a particular character, all the principal terms being susceptible of augmentation by one equivalent of hydrogen, so that two parallel groups may be formed, of which the following examples will give an idea:—

Indigo blue, $C_{16}H_5NO_2 + H = C_{16}H_6NO_2$, or Indigo; white Isatine, $C_{16}H_5NO_4 + H = C_{16}H_6NO_4$, or Isathyde; Chloride of Isatine, $C_{16}H_5ClNO_4 + H = H_{16}H_6ClNO_4$, chloride of isathyde; Isatic Acid, $C_{16}H_5NO_4 HO + H = C_{16}H_6NO_4HO$, Hydrindine.

*Indigo blue*, $C_{16}H_5NO_2$ (Indigotine).—Indigo exists in several plants. The indigo of commerce contains about 45 per cent. of pure indigo; the remainder of the article, consisting of ill-defined extractive, resinous and gummy matters, fecula and saline principles, silica, alumina, oxide of iron, carbonate of lime, &c. The indigo of commerce is purified by powdering it and washing it successively with boiling distilled water, alcohol, and water acidulated with hydrochloric acid. To obtain indigo pure, into a stoppered flask holding rather more than 10 pints, about 1850 grains of indigo are to be introduced;

then about 2,900 grains of a concentrated alcoholic solution of soda, and the flask is to be filled up with boiling alcohol of 75 per cent., saturated with grape sugar. The whole is to be well shaken; the flask closed and left to itself. The indigo dissolves, and affords a liquid of a deep reddish yellow. When this liquid is clear, it is decanted into an open vessel. The indigo blue, which was reduced and converted into a soluble white indigo, is oxidated afresh, passes from red to violet, then into a splendid blue, and in this slow formation it crystallises. It is washed with boiling water and alcohol, and then dried. Indigotine is also obtained, when indigo is heated in a glass tube through which a current of hydrogen is passed, in fine crystalline needles. It may also be prepared by heating indigo between the lids of two platinum crucibles, when fine crystals form on the upper plate.

Indigotine is not altered by exposure to the air; it is insoluble in water. Alcohol dissolves very little of it, with the aid of heat and pressure. It is insoluble in water and ether, dilute acids, and alkalies. Its crystals are plates, or six-sided prisms. When carefully heated it is volatilised at 554° without residue. It is without smell or taste. It is soluble in sulphuric acid, forming a compound. When placed in contact with water and a substance having a strong affinity for oxygen, it decomposes the water, taking the hydrogen. Thus hydruretted, it forms the white indigo, *indigogene*. The alkalies, sulphur, phosphorus, and many metals have this property; also starch, gum, tannine, &c. This change also takes place when blue indigo is introduced into a mixture of three parts of alcohol and two of sulphuric acid.

*Action of Sulphuric Acid on Indigo.* Sulphindelic acid, $C_{16}H_5NO_2$. $2SO_3$, or $C_{16}H_4NO2SO_3,HO$. The action of sulphuric acid on indigo, yields different results according to the degree of concentration of the acid, and the length of time the action endures. Sulphuric acid dissolves most indigo when concentrated, and the Nordhausen acid is best fitted for the purpose. As soon as the indigo is dissolved, it is combined with the acid; but if the proportion of strong sulphuric acid has not been more than five times the weight of the indigo, and if the contact has not been very prolonged, a compound, known as indigo purple, is formed, composed of 1 eq. of indigo and one of sulphuric acid; when a larger quantity, say 20 of the ordinary commercial strength, and 8 or 10 parts of the Nordhausen, then a substance is formed called carmen of indigo, a compound of 2 cqts. of acid and one of indigo. When indigo is left long in contact with deoxidating agents, it undergoes a great change in its physical properties, it becomes soluble, and nearly colourless, and is precipitable from alkaline solutions as a white flocculent substance, which, on exposure to the air, rapidly becomes blue. It is on this principle that dyeing with indigo is conducted. One part of powdered indigo, 2 of green copperas, 3 of slaked lime, and 12 of water are mixed together, and left to stand. The protosalt of iron, in becoming a persalt, reduces the indigo; a yellowish solution is obtained. Acids precipitate the white indigo from this solution in a form which quickly absorbs oxygen from the air and becomes blue, and cloth steeped in it exposed to the air undergoes a similar change.

*Isatine*, $C_{16}H_5NO_4$, is prepared by taking one part of indigo, one of bichromate of potass, and one of sulphuric acid, with 25 of water, and heating the mixture until carbonic acid is evolved; a deep brown solution is formed, which on concentrating slightly, and cooling, yields yellowish red rhombic prisms of isatine, which are to be purified by recrystallisation. Isatine is unalterable in the air, inodorous, nearly insoluble in cold water; soluble in boiling water and alcohol. When heated, it melts and gives off acrid vapours. When isatine is acted on by chlorine, it forms *chlorisatine* by a substitution of an atom of chlorine for one of hydrogen; and by a further action of chlorine, *bichlorisatine* is formed. Bromine has a similar action. When an excess of chlorine is passed into an alcoholic solution of chloride of isatine, chloranile, the extreme term of the action of chlorine on the salicylic series is formed, $C_6Cl_2O_2$, it forms in pearly scales, and by boiling with potass forms *chloranilic acid*. When a hot solution of isatine is treated with hydrosulphate of ammonia, a deposit of sulphur takes place, and a white crystalline substance is formed, *isathyde*, $C_{14}H_6NO_4$. Ammonia forms with isatine compounds containing the azote of the ammonia and that of the indigo. When isatine is dissolved in solution of caustic potass in the cold, it assumes a purple colour, but undergoes no change, and can be precipitated from the solution by acids; when boiled for some time, however, the solution changes its colour, and, on evaporation, affords crystals of the isatinate of potass. This acid, obtained free, is a white, somewhat crystalline powder.

*Indigogene.* White indigo, $C_{16}H_5NO_2H$, is obtained by the action of one part of powdered indigo, three of slaked lime, two of green copperas, and 150 of water on each other, in a vessel from which air is excluded. The solution, after a day or two, is to be drawn off by a syphon into a vessel filled with carbonic acid, and containing enough acetic or muriatic acid, saturated with sulphurous acid, to more than saturate the lime contained in the mixture. At the contact of the two liquids, white or grayish flocculi are precipitated, which are to be collected on a filter and quickly washed; at first with cold water saturated with sulphurous acid, and then with pure water. The filter charged with the matter is to be first placed between folds of blotting paper, and then between two dried bricks above sulphuric acid *in vacuo*; it is then to be kept in an atmosphere of carbonic acid. It is a white crystalline, silky solid, heavier than water, inodorous and insipid, insoluble in water, soluble in alcohol and ether. When heated, in contact with air, it instantly assumes a deep purple tint; heated *in vacuo*, it is decomposed, forming indigo blue, water, and a blackish residue.

*Isathyde*, $O_{16}H_6NO_4$, bears the same relation to isatine that indigo white does to indigo blue, and is obtained by subjecting the isatine to reducing agents. This is done by forming a hot alcoholic solution of isatine, and while it is hot, pouring in a little hydrosulphate of ammonia. The mixture is then left to itself, and in the course of a few days deposits octahedral crystals of sulphur, and white lamellar or prismatic crystals of isathyde. It is softened by heat, and becomes violet

brown before decomposition. It is inodorous and insipid, insoluble in water, slightly so in boiling alcohol and ether.

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### SECT. VIII.—MISCELLANEOUS ANALOGOUS SERIES.

*Phloridzine*, $C_8H_5O_4$. Very similar to salicine; is obtained from the fresh rind of the roots of the apple, cherry, and prune. It is obtained by digesting the rind with weak alcohol, evaporating and crystallising the phloridzine, purifying by boiling with animal charcoal and recrystallisation. It crystallises in silky woven needles, soluble in 1,000 parts of cold water, and very soluble in hot water; in alcohol and wood spirit in all proportions. Very slightly soluble in ether. Its taste is bitter. By the action of a weak mineral acid, it is converted into grape sugar, and a substance called phloretine,—a white substance, which crystallises in plates.

*Cumarine*, $C_{18}H_6O_4$, is obtained from the tonko bean, where it often occurs crystallised *native*. It is obtained from the sliced beans in the way in which phloridzine is obtained from cherry-root bark. It is a fragrant substance, convertible, by the action of nitric acid, into picric acid. Cumaric acid is formed when cumarine is treated with a lye of potass.

#### ANISIC SERIES OF COMPOUNDS.

This series is founded apparently on a carburetted hydrogen of the type $C_{14}H_8$. They are obtained principally from oil of aniseed, balsam of tolu, and the volatile oils of other plants. The substance of the formula $C_{14}H_8$, called *benzoene, anisene*, or *tuluole*, is prepared by distilling the resin of tolu repeatedly, and rectifying the product of the distillation from chloride of calcium, at a temperature between 270° and 280°. It very closely resembles benzine.

*Anisole*, $C_{14}H_8O_2$, is produced by distilling anisic acid with baryta, by the removal of carbonic acid for $C_{16}H_8O_6$, anisic acid $= C_{14}H_8O_2 + 2CO_2$. It is a colourless aromatic fluid, insoluble in water, soluble in alcohol and ether, which boils at 305°.

*Anisic Acid*, $C_{16}H_8O_6$, or $C_{16}H_7O_5HO$, or $C_{16}H_7O_4O.HO$, hydrate of the oxide of the hypothetical radical anisyle, is prepared by boiling the essence of aniseed or tarragon with nitric acid. In cooling, crystals of anisic acid are formed, which should be washed with water and sublimed. It crystallises in needles, which are slightly soluble in cold water, more so in hot water, alcohol, and ether. It sublimes at 347°, without decomposition.

*Hydruret of Anisyle*, $C_{16}H_8O_4$, or $C_{16}H_7O_4,H$, is formed by distilling the essence of aniseed with weak nitric acid. A red oil is formed at the bottom of the nitric acid. This is to be collected and distilled. It leaves a carbonaceous residue, and furnishes two substances,—a crystalline solid, anisic acid, and a liquid, the hydruret of anisyle. To show the analogy between anisene or toluole and benzine, a substance

analogous to aniline, possessed of basic properties, is formed from the action of ammonia in alcohol, and sulphuretted hydrogen on toluole. This is toluidine, $C_{14}H_9N$, or $C_{14}H_7,NH_2$.

*Creasote*, $C_{14}H_{16}O_4$. Isomeric with anisyle. Is prepared by distilling oil of wood tar until it has obtained the consistence of pitch, or until the white vapours of paraffine begin to appear. The liquid which passes into the receiver, divides into three layers, of which the inferior contains the creasote. This is to be collected and saturated with carbonate of soda, left to repose, and the new oil which separates, decanted. This product being anew distilled, gives at first products lighter than water. These are rejected, and when a heavy oil comes it is set aside; it may now be agitated with phosphoric acid, to get rid of ammonia, and again distilled. Finally it is to be dissolved in a solution of potassa of sp. gr. 1·12, an oil floats on the top, and the fluid below is decanted. The alkaline solution is boiled, and left in contact with air, and decomposed with sulphuric acid. The creasote is then separated, and decomposed by acid; and this is repeated until the creasote ceases to be coloured on exposure to air. It is then well washed and distilled, and the first product of the distillation rejected. Creasote is quite neutral. Its odour is peculiar, and its taste burning. Its sp. gr. is 1·040; it boils at between 398-9°. It is hardly soluble in water, soluble in alcohol and acetic acid, oils, and essences. It dissolves several fatty substances. It corrodes the tongue, cauterises the tissues, coagulates albumen, and prevents the putrefaction of meat. It dissolves several salts, especially chlorides, and reduces some of the metallic salts. Treated with chlorate of potass and muriatic acid, it yields chloranile. Nitric acid converts it, with a prolonged boiling, into several crystallisable substances, among others oxalic and picric acids.

### CINNAMIC SERIES.

In this series there are three terms of the preceding series. Cinnamine or cinnamole, isomeric with benzine, $C_{16}H_8$, and uniting like it with carbonic oxide to form the hydruret of the imaginary radicle cinnamyle, analogous to the hydruret of benzoyle, and with carbonic acid to form cinnamic acid, which is thus analogous to benzoic acid. Thus the three principal formulas of the series are—

| | |
|---|---|
| Cinnamine . . . . . . . | $C_{16}H_8$ |
| Hydruret of cinnamyle . . . | $C_{18}H_8O_2 = C_{16}H_8, C_2O_2$ |
| Cinnamic acid . . . . . . | $C_{18}H_8O_4 = C_{16}H_8, C_2O_4$ |

The formula for cinnamyle is assigned to be $C_{18}H_7O_2$, which makes oil of cinnamon ($C_{18}H_7O_2,H$) and cinnamic acid ($C_{18}H_7O_2,O,HO$), or the hydrate of the oxide of cinnamyle, as benzoic acid is made the hydrate of the oxide of benzoyle. The symbol used for cinnamyle is Ci. Cumarine differs from the hydruret of cinnamyle only by the substitution of two equivalents of oxygen for two of hydrogen.

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|---|---|
| Hydruret of cinnamyle . . . . . . | $C_{18}H_8O_2$ |
| Cumarine . . . . . . . . . . | $C_{18}H_6O_4$ |

*Cinnamine, Cinnamole, Styrole,* $C_{16}H_8$, is obtained, by several processes, from the distillation of dragon's blood, by distilling styrax with carbonate of soda, or by the distillation of cinnamic acid with lime or baryta in the proportion of 1 of the former and 4 of the latter. It is a colourless fluid, insoluble in water, soluble in alcohol and ether, possessed of a penetrating smell and of a burning aromatic taste. It boils at 294°. When heated in scaled tubes above its boiling point, it is converted into a solid *metacinnamene.* It combines with peroxide of azote, and chlorine and bromine, forming well-defined principles.

*Hydruret of Cinnamyle* (cinnamon oil), $C_{18}H_8O_2$, is prepared by crushing cinnamon, infusing it then for several hours in salt water, and then distilling the whole. The essential oil is separated from the rest of the fluid, which passes over, and is dried by means of chloride of calcium. It is an oily fragrant substance, which is solidified by the addition of nitric acid, forming a hydrate of nitrate of the hydruret.

*Cinnamic Acid,* $CiO,HO$, or $C_{18}H_7O_2,O,HO$, exists free in balsams of tolu and Peru. It may be prepared very directly by exposing oil of cinnamon to the action of oxygen. It may also be obtained by dropping Peru balsam into milk of lime, at the boiling point; the balsam combines with the lime; the mass formed, exhausted by a large quantity of boiling water, yields crystals of cinnamate of lime, and this, decomposed by hydrochloric acid, yields cinnamic acid, which crystallises in white pearly scales or prisms from its solutions in boiling water or alcohol. Its sp. gr. is 1·245. In the mother liquid much benzoic acid remains after the separation of the cinnamate of lime. The crystals of cinnamic acid are smaller than those of benzoic acid. It fuses at 248°, and is distilled at 560°. Its vapours are very irritating. It is very soluble in alcohol; less so in water than benzoic acid. Distilled with excess of lime and baryta it yields cinnamine. Its salts are very similar to the benzoates. When cinnamon oil is acted on by nitric acid, it is decomposed, hydruret of benzoyle and benzoic acid being formed.

### GUAIACIC SERIES.

*Tolene* or *Guaiacene,* the root of this series, has the formula $C_{10}H_8$, and corresponds to benzine, guaiacyle to the hydrate of phenyle, and guaiacic acid to salicylic acid. The first of these is obtained by keeping for a long time the crude essence of tolu at a temperature of 320°; then by distilling the balsam, which separates with water, and finally distilling from potassa. It is a colourless fluid liquid. Guaiacene, $C_{10}H_8O_2$, is one of the products of the dry distillation of guaiac. Guaiacic acid, $C_{12}H_8O_6$, is obtained by dissolving the resin of guaiac in alcohol, evaporating this to a third, then leaving the solution to rest. Resin is deposited, the solution is neutralised by baryta, and the barytic salt purified by crystallisation and decomposed by sulphuric acid. The soluble guaiacic acid exists in the solution, which is evaporated, the residue exhausted by ether, which, on evaporating, affords crystals of guaiacic acid; these, on being sublimed, afford crystals

closely resembling benzoic acid. Guaiacic acid is very soluble in water, alcohol, and ether.

### CUMINIC SERIES.

Of this series, derived from cumin oil, there are several analogous compounds to the benzine group. Here the hydrocarburet is $C_{18}H_{12}$, of which *Cumene* is the example. It is prepared in the same way as benzine, viz., by distilling a mixture of crystallised cuminic acid with baryta. It is a colourless fluid, which boils at 304°. *Cuminole*, $C_{20}H_{12}O_2$, is the least volatile part of oil of cumin. *Cuminic acid*, $C_{20}H_{11}O_3HO$, is obtained by dropping oil of cumin on melted potass in a retort, and decomposing the cuminate of potass, formed in solution by nitric or muriatic acid. It is deposited in flocculi, which can be crystallised from alcohol. These sublime like benzoic acid, to which cuminic acid is analogous. In the process, when the cuminic oil is dropped upon melted potass, a substance is sublimed called *cymene*, which is cumene with the addition of $C_2H_2$. The hypothetical radicle of this group is cumyle, $C_{20}H_{11}O_2$, of which cuminic acid would be the hydrate of the oxide.

Essence of cloves produces *eugenine*, and eugenic and caryophyllic acids, and the number of these substances might be much augmented.

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# CHAP. 6.—ESSENTIAL OILS, RESINS, AND ANALOGOUS SUBSTANCES.

### SECT. 1.—ESSENTIAL OILS CONTAINING SULPHUR.

These are chiefly oils of mustard and garlic, also horse-radish and cochliaria, and doubtless onion. In several other vegetables the presence of oils containing sulphur is supposed. These oils practically may be reduced to two, essence of garlic and essence of mustard; and the essence of garlic is made out to be an organic sulphuret, of which the essence of mustard is the sulphocyanuret. The formula for allyle, the supposed hypothetical radical, is $C_6H_5$, while oil of garlic is $C_6H_5S$, or AllS, and oil of mustard, $C_6H_5S,C_2NS$.

*Essence of Black Mustard* is obtained first by expressing from the grain the fat oil which it contains, then moistening it with water, and leaving it to itself for several hours. A fermentation takes place.

After a sufficient contact, distillation is proceeded with, and watery vapours condense, carrying with them an oil heavier than water. By repeated distillation, and at last at a temperature between 256° and 311°, an oil somewhat heavier than water passes, which has for formula $C_3H_5NS_2$. It is colourless, or slightly yellow, with an acrid odour,

and a vapour which irritates the eyes; boils at 289°. Water slightly dissolves it; it is very soluble in alcohol and ether. When acted on by ammonia, it forms a substance thiosinamine, which has all the characters of an organic base, whose formula is $C_8H_8N_2S_2NH_3$; this, when acted on by metallic oxides, yields a body free from sulphur called sinnamine. The fermentation, from which the oil of sulphur is formed, is promoted by the presence of an albuminous principle analogous to synaptase, *myrosine*. This is obtained from white mustard, in which it exists, as well as in the black variety, by digesting it in cold water, evaporating the infusion to a syrup below 100°, then precipitating by alcohol, re-dissolving the precipitate in alcohol, and evaporating to dryness. Myronic acid is an acid syrup existing in the mustard seed—little known—by the mutual action of which, and myrosine, the oil is supposed to be formed. By mixing oil of garlic with caustic soda, and quick-lime, and heating them in a sealed tube at a temperature above that of boiling water, the *oxide of allyle* is formed.

## SECT 2.—ESSENCES AND ESSENTIAL OILS.

Essential oils are distinguished from fixed oils by the rapidity with which they evaporate when dropped on a piece of blotting paper. Being obtainable by distillation, they are called volatile oils. They exist in the pores or cells of several parts of plants, and are mostly extracted by distillation of these with water at the temperature of 212°, although this is mostly below the boiling point, but they are partly carried over mechanically and condense with the steam. They consist of a solid portion, stearoptene, and a fluid portion, oleoptene. The former may be separated by cold and pressure. They are generally divided into two classes,—the hydrocarburetted oils, and the oxygenated; the former formed on the type of oil of turpentine. Their formula is some modification of $C_5H_4$. The oxygen oils have various formulas. Camphor, $C_{20}H_{16}O_2$, is a body of the same character as the oxygenated essential oils. To these various principles it would be impossible to do justice within these limits. Some may be selected as examples of the rest.

*Oil of Turpentine*, $C_{20}H_{16}$. Several species of pine allow a substance like honey to exude, which is turpentine. It contains the oil or essence mixed with resin and other impurities. When this or other parts of the plant are distilled with water, they yield the essential oil, which is purified by repeated distillation. Its natural qualities are well known. Its sp. gr. is 0·865, and it boils at 312°. It is almost insoluble in water, more soluble in alcohol and ether; much of its use is owing to its mixing in all proportions with fixed oils; as for instance in painting; nitric acid and chlorine act on it with great violence, often producing combustion. When dry muriatic acid gas is passed into it, surrounded by a freezing mixture, an artificial camphor is formed, whose formula is $C_{20}H_{16}$, HCl, or muriate of oil of turpentine. This can be purified by solution in alcohol. It is neutral, sublimes, and does not pre-

cipitate nitrate of silver. When this substance is distilled with lime, an isomeric compound of oil of turpentine passes over. An isomeric liquid compound of the same composition as that of the solid muriate exists in the mother liquids whence the solid is derived, and they on being distilled yield one or more compounds isomeric with oil of turpentine. By distilling oil of turpentine with sulphuric acid, another isomeric compound of oil of turpentine termed colophene may be formed. The essential oils isomeric with oil of turpentine are known generally as *camphene*; but the isomeric compounds obtained by distilling the solid and fluid muriates with lime, are termed respectively camphylene and terebylene. At some degrees below zero, turpentine deposits prismatic crystals, which are a white hydrate of turpentine containing 6 eqts. of water.

The same substance is formed by the action of dilute nitric acid, sp. gr. 1·25, or 1·3, in essence of turpentine, with alcohol of 80 per cent. They are mixed in the proportion of 2 parts of the first, 8 of the second, and 1 of the third. The mixture is to be shaken until the crystals of the hydrate appear, then left quiet at a temperature of a little above 70°. In the course of several days the crystals continue to form. They are to be drained, and then dissolved in boiling water, and treated with animal charcoal. On cooling, prismatic colourless crystals separate, of the formula, $C_{20}H_{16}$,6HO. The other essential oils of this class closely resemble the essence of turpentine.

### OXYGENATED ESSENCES.—CAMPHORS.

*Common Camphor—Camphor of Japan*, $C_{10}H_8O$, is obtained by distilling the wood of the laurus camphora with water. It exists also in several of the labiata. It is refined by redistillation with a little quick lime. Its ordinary physical characters are well known. It melts at 347° and boils at 400°, but before boiling it volatilises, in fact it does so at ordinary temperatures. It is soluble in about 1,000 parts of water and the same of alcohol, and is precipitated from its solution in the former on the addition of water. It evaporates more quickly in water than in air, exhibiting curious motions at the same time. Ether and essential oils dissolve it readily; also fatty oils. It burns with a smoky flame. When its vapour is decomposed by heat, in contact with iron, it yields naphthaline and a hydrocarburet isomeric with benzine. In contact with red-hot lime it is decomposed into a variety of substances. Exposed to a current of muriatic acid it absorbs it and forms a transparent, colourless liquid, isomeric with hydrochlorate of oil of turpentine.

*Camphoric Acid*, $C_{10}H_7O_3$,HO, is prepared by heating camphor with 10 times its weight of nitric acid, and condensing the products of the distillation, and redistilling several times. On evaporation the acid liquor deposits camphoric acid. It is purified by dissolving it in carbonate of potass, evaporating to dryness, and precipitating the camphoric acid by nitric acid. It crystallises from its solution in boiling water in scales or needles. It melts when heated, losing its water. When the

camphorate of lime is distilled it yields a volatile yellowish oil *phorone*, $C_9H_7O$, or $C_{18}H_{14}O_2$. Acted on by phosphoric acid this loses water and forms *cumole*.

When camphor vapour is directed upon a mixture of potass and lime at the temperature of 750° under pressure, and the alkaline mass exhausted by boiling water acidulated with nitric acid, a white crystalline acid mass is obtained, which is to be washed and dried: this is campholic acid, $C_{20}H_{18}O_4$, which crystallises from its solution in alcohol. This distilled with dry phosphoric acid yields *campholene*, an oily liquid isomeric with camphene, $C_{18}H_{16}$; and when the campholate of lime is distilled it gives product to au oily liquid, campholone, $C_{19}H_{17}O$.

*Borneo Camphor*, $C_{10}H_9O$, occurs in two forms, solid and fluid. The solid is composed of crystalline fragments, transparent and fusible, which have an odour between camphor aud pepper, and a hot taste. It is about the weight of water, and not soluble in it.

The essence of valerian, rectified from a very concentrated lye of potass, allows a carburet of hydrogen to be distilled, isomeric with the hydrocarbon, the base of turpentine, and very similar to it. The fluid Borneo camphor is a solution of the solid in this substance, which is termed *borneene*.

Numerous essential oxygenated oils, as essence of mint, of cedar, of rue, absinthe, cajeput, &c., present strong analogies with camphor.

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### SECT. 3.—CAOUTCHOUC AND GUTTA PERCHA.

*Caoutchouc*, $C_8H_7$, is found in several plants, but is obtained chiefly from siphonia elastica and from curccola elastica and urostigma elastica, in Guiana and India. It occurs in several species of euphorbia, and principles aualogous to it exist in fossil plants. It is obtained by making iucisious in the trees, whence the juice exudes. This juice contains about 40 per cent. of solid matters—caoutchouc, albumen, extractive, &c. The juice is dried in clay moulds. To accelerate the desiccation they are exposed to the flames of branches of trees, whose smoke gives a dark colour to the caoutchouc. Otherwise the colour of caoutchouc is yellow. Pure caoutchouc is almost white and translucent; sp. gr. 0·925; melts at 455° and becomes viscous. Heated further, it gives off vapours which burn in the air with a smoky flame. By dry distillation it yields several hydrocarburets.

It is not acted on by chlorine, iodine, hydrochloric acid, fluosilicic acid, and ammonia. Sulphuric acid ouly cleans its surface. Commercial nitric acid ouly yellows it, but it is powerfully acted on by fuming nitric acid. Bisulphuret of carbon, the oils produced in the distillation of coal, the liquid hydrocarburets which are formed in the solution of caoutchouc itself, are the best solvents. Coal-tar naphtha, on account of its cheapness, is the substance generally employed, and with it those

various waterproof substances so generally used are made. Sheets of india-rubber are vulcanised by exposing them to the vapour of sulphur, or immersing them in melted sulphur. Vulcanised india-rubber is also made by dissolving 25 parts of caoutchouc in an essential oil, and grinding it with 7 of white lead and 5 of sulphur, like a paint. The numerous uses of this substance are well known.

*Gutta Percha* is obtained as a milky juice from Icosandra gutta in much the same way as caoutchouc; sp. gr. 0·979; composition C 87·8, H 12·2*. It softens at 122°, and owes its very valuable properties, in great part, to its capability of being worked into moulds, at between 158° and 176°. Its solvents are nearly those of caoutchouc, and it can be vulcanised like it.

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### SECT. 4.—RESINS.

These are principles very widely spread existing in more or less quantity in almost all parts of plants, but in such variable proportions that sometimes their presence is imperceptible, whereas at other times they exude spontaneously either alone or through incisions, accompanied by an essential oil which either lowers their point of fusion or keeps them entirely dissolved. The essential oil having been driven off by distillation, as already shown, the resin remains. When the resin is less abundant, the organic tissue containing it is to be treated with strong alcohol, which takes up the resin, and from which it can be precipitated by the addition of water. Resins are solid, not volatile, almost always translucent, colourless, or tinged yellow, brownish, red, or greenish blue. They rarely crystallise, are insoluble in water, soluble in alcohol, ether, and essential oils. Some are soluble in alkaline solutions, and form, by double decomposition with metallic salts, a kind of compound with metallic oxides, and hence are deemed acid ; others are neutral. Muriatic acid has little action on them. Sulphuric acid dissolves them in the cold, and when heated, sulphurous and carbonic acids and carbonic oxide are given off, and a carbonaceous matter remains, which has been called artificial tannine. Nitric acid causes the formation of a great many principles,—phenic acid from the resin of xanthoroea hostilis, chrysammic acid from aloes. The pyrogenous products are generally carburets of hydrogen, carbolic acid not unfrequently, also benzoic and cinnamic acids. The resins are generally regarded as products of the oxygenation of the essences; the latter, when exposed to the air, absorb oxygen, and to a certain extent are resinified.

The different species of pine afford a soft resin, which affords essence of turpentine on distillation with water, and leaves a residue which is called rosin, or *colophane*. This is composed of several acid

* The formula would be probably that of caoutchouc.

principles, which have been termed pimaric, silvic, and pinic acids. These acids are isomeric, having the formula $C_{40}H_{30}O_4$.

*Pimaric Acid* is obtained from the terebinthine of the pine of the Landes, which is in white masses like suet, composed chiefly of granular crystals of pimaric acid. This is divided into fragments, on which a mixture of five or six of alcohol to one of ether is thrown. The mixture is bruised in this, and then washed once or twice with the same mixture. Pimaric acid remains undissolved, and is purified by dissolving it and crystallising it two or three times from boiling alcohol. These crystals are prisms with rectangular bases. It is very soluble in ether and boiling alcohol. It melts at 257° and then undergoes an isomeric change which renders it more soluble in cold alcohol, although the pimaric acid is so soon regenerated that the liquid is filled with crystals of it.

*Silvic Acid* is obtained by the distillation of pimaric acid, when an oily matter is found in the beak of the retort, which readily dissolves in boiling alcohol, and crystallises in triangular tables. Pimaric acid kept in alcohol, in crystals, becomes yellow after some months, translucent and friable, and has passed into the third modification of pimaric acid—*pinic acid*. Pinic and sylvic acids, as they exist in resin, may be separated by their solubility in alcohol, the former being much the more soluble of the two—in its own weight of cold alcohol. Of the numerous resins known in commerce, it may be stated that *lac* is harder than colophane and very soluble in alcohol. Copal differs from the other resins in being with difficulty soluble in alcohol and essential oils ; but mixable when melted with oils and thus made into a varnish. Balsams are natural mixtures of resins and essential oils.

### PRODUCTS OF THE DRY DISTILLATION OF OILS, CAOUTCHOUC, RESINS, WOOD, AND COAL.

Oils that would not be otherwise used are employed for the manufacture of gas. They are putrid oils, crude oils of grains, and oils obtained in the dressing of wool. They are decomposed at a dull red heat in a cast iron cylinder containing pieces of stone or coke. The gases disengaged are carbonic oxide, light and heavy carburets of hydrogen, and hydrogen ; of these the hydrocarburets furnishing 80 or 85 per cent. When the gaseous products are compressed to about $\frac{1}{30}$th of their volume, a quantity of a very volatile liquid is formed. This fluid contains benzine and two other hydrocarburets. This liquid exposed to the air, immediately abandons the more volatile hydrocarburets. At 100°, if the heat is continued, only $\frac{1}{10}$th of its volume is lost ; if the heat is still continued, the boiling point rises and necessarily remains some time between 172° and 188°, and finally rises to 248°. The product distilled about 185°, condensed in a freezing mixture, becomes half solid, and by expressing, cooling, and recrystallising the mass, it is found to have the formula of benzine, $C_{12}H_6$. The liquid whence the benzine is deposited boils steadily at 185°, and is not congealed at zero. Its formula appears to be $C_8H_8$. The first 10th distilled, condensed by

intense cold, forms a liquid which boils below zero. The most volatile part of all consists of a gas isomeric with olefiant gas, and has the formula $C_8H_8$; it has been termed quadrocarburet of hydrogen.

*Distillation of Caoutchouc.*—Caoutchouc of commerce contains 13·7 per cent. of water, which it loses when dried over sulphuric acid. If dried caoutchouc be submitted to destructive distillation, it gives off first volatile ammoniacal products, whose presence is due to the albumen mixed with the caoutchouc. The caoutchouc then boils, and oily matters pass over = $\frac{9}{12}$ths of the caoutchouc. At first the oil is yellowish, then brown, and then black. A carbonaceous mass is left in the retort. When these oils are condensed separately by great cold, it is found that the extreme products have the composition of olefiant gas, and the intermediate of essence of turpentine. In the most volatile portion are quadrocarburet of hydrogen, and an oil, *caoutchene*, crystallising by extreme cold, also isomeric with olefiant gas; in the least volatile part, an oil, isomeric also with olefiant gas, boiling about 600°, and not solidifying by cold, called *heevine*, has been discovered. The intermediate products have all a resemblance to essence of turpentine.

The dry distillation of resins gives rise to substances isomeric with cinnamon, benzoine, benzine, and naphthaline.

The dry distillation of wood yields most complex products, some of which have already been spoken of, as acetic acid, methylic compounds, creasote, &c. The same applies to the products of the distillation of coal; three of the most important, not yet described, are paraffine, eupione, and pyrene.

*Paraffine*, $C_{48}H_{30}(C_{20}H_{21})$, is obtained both from wood, tar, and from the products of the dry distillation of bees-wax. The distillation of brushwood, too, gives three layers of liquid in the receiver; the bottom layer, containing paraffine dissolved in an oily liquid, is re-distilled, and as soon as the temperature becomes elevated, paraffine begins to pass over. The product is received in its volume of alcohol of 83 per cent., and 6 or 8 volumes more of alcohol added. The paraffine is then precipitated in plates, which are purified by washing. It is best crystallised from ether.

It crystallises in needles or colourless pearly plates, is insipid and inodorous. It melts at 102°, and distils without alteration at 590°. It burns with a bright white flame, without smoke; is insoluble in water, soluble in ether and essential and fat oils. It is little attacked by chemical agents. It is found in the dry distillation of fatty bodies and bitumen.

*Eupione*, $C_5H_6$, is obtained from the most volatile of the three layers in the distillation of wood-tar, already mentioned. This is mixed with the third of its volume of strong sulphuric acid; the mixture is shaken, and the eupione comes to the surface. This treatment is renewed, a little nitric acid being added. Then it is washed with an alkaline lye, and distilled along with water, till three-quarters of the light oil have passed over; the eupione is then dried, and finally rectified from potassium. Eupione is colourless and tasteless, but with

an agreeable smell. It is the most fluid of all liquids; sp. gr. 0·655. It is insoluble in water, slightly soluble in weak alcohol, and in all proportions in strong alcohol. It boils at 117°.

*Pyrene,* $C_5H_2$, the least volatile part of tar contains *chrysene,* which can be purified by washing with ether. The ether takes up pyrene. When the ethereal solution of pyrene is cooled to zero, the pyrene is deposited in crystals. These are expressed, the one-fifth distilled off, and the product anew treated with ether, and redissolved in boiling alcohol. It is a powder, composed of minute rhomboidal tables. Melts at 347°.

*Chrysene* is a yellow powder, whose formula is $C_{12}H_4$. Melts at 450°. The difference between the products of the distillation of coal-tar and wood-tar consists principally in this, that the hydrate of oxide of phenyle, or carbolic acid, replaces creasote, and that pure aniline, naphthaline, picoline, and pyrrhole abound.

Picamare is a colourless bitter oil in wood-tar; capnomare a colourless oil, with the smell of resin, from the same source; and pittacal an indigo-coloured substance.

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### SECT. 5.—ORGANIC FOSSILS.

The fossils of plants still exhibit the remains of their chemical characters, metamorphosed, it is true, but often retaining sufficient traces of their source.

*Amber* is found mingled with lignites in deposits of plastic clay, and in the inferior part of cretaceous districts, principally on the southern shores of the Baltic. It is supposed to proceed from a resin similar to turpentine. It is found in nodules. Sp. gr. about 1·070. Its physical properties, and also its electrical, are well known. Is insoluble in water. Absolute alcohol and ether dissolve ten or twelve per cent. of it. Besides succinic acid, it contains a volatile oil and two resins. When distilled with water, the resins come on the top, a volatile oil is distilled, and succinic acid remains in solution. The part insoluble in ether is termed bitumen of amber. The oil of amber is $C_{20}H_{16}$. Nitric acid gives a yellow resin with amber, which has the odour of musk, and which is called artificial musk.

*Resin Asphalt,* or *Retinasphalt, Retinite,* are names given to several fossil products, generally of a pale brown or ochrey colour, having some such composition as represented by the formula $C_{21}H_{14}O_2$.

Several fossil fats exist.

### ASPHALT, BITUMEN, PETROLEUM.

The principal differences between these substances arise from their respective degrees of solidity,—the first being solid, the second having less consistence, and the third being liquid; but the terms bitumen and asphalt are often employed as if they were synonymous;

and the bitumens can be brought to the consistence of the asphalts, by chasing off the oily matters which they contain. These products · are, for the most part, in relation with considerable deposits of organic materials in decomposition; they communicate with layers of coal; they have been found with the tertiary lignites, sometimes flowing from volcanic strata, at other times floating on the surface of lakes. Asphalt resembles coal internally, but its fracture is bright; sp. gr. about 1·02. It melts at the temperature of boiling water. The asphalt contains an oil called petrolene, whose formula is C H$_8$, isomeric with essence of turpentine. Either the natural asphalt, or that procured from gas works, is now used extensively, mixed with sand, lime, &c., as a concrete.

*Bituminous schists* contain small quantities of carbon, comparatively large quantities of oil, as much as 14 per cent., and large quantities of earthy substances.

*Petroleum, Naphtha.* The former name is given to the darker coloured, the latter to the lighter hydrocarburetted oils of mineral origin. They owe colour to the presence of organic matters. When rectified there is no difference. They seem to be solutions of paraffine in different oils and vary in composition; that of the Persian naphtha is given $C_6H_5$. Persian naphtha is nearly colourless. Sp. gr. 0·758. Boils at 320°. The use of it to preserve potassium, on account of its containing no oxygen, is well known.

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# CHAP. 7.—ARTIFICIAL ORGANIC BASES.

A SERIES of substances exist, possessing striking relation to the organic bases of vegetable origin, but which can be formed artificially, from the ordinary ammoniacal salts and organic substances of which mention has been already made; in these compounds, the radicals before alluded to displace a certain number of equivalents of the hydrogen of ammonia. The bodies which effect these changes are chiefly the alcoholic compounds already described.

ETHYLAMINE, $C_4H_7N$, or $NH_2C_4H_5=AeNH_2$ (Amide of Ethyle), is formed by heating bromide or iodide of ethyle with alcoholic spirit of ammonia. The bromide of ethyle (hydrobromic ether) is best prepared by distilling 8 parts of bromine, 32 of alcohol, and 1 of phosphorus. On digesting the bromide with alcoholic solution of ammonia, the ammonia is gradually neutralised or volatilised, and on evaporating the solution by a water bath, a crystalline compound of bromine and ethylamine is obtained, which being digested with caustic lime yields ethylamine, good means of condensation being employed. Ethylamine is a volatile fluid; sp. gr. 0·69; boils at 68°. It may also be obtained by the action of potass on cyanate of ethyle.

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It has the smell and many of the reactions of ammonia; reddens turmeric; gives a white cloud with muriatic acid fumes; and precipitates metallic salts like ammonia, yielding a bluish precipitate with salts of copper, soluble in excess of ethylamine. It has also a great attraction for water. The chief test by which it may be distinguished from ammonia, is the combustibility of its vapour; with chloride of platinum, it forms two platinum bases; treated with chlorine, it yields the chloride of ethylamine, and a yellow liquid which gives off penetrating fumes of the composition $NCl_2C_4H_5$. With cyanic acid, ethylamine yields a substance analogous to urea. When ethylamine and bromide of ethyle are heated together in a sealed tube for several hours, they form a crystalline mass, which, distilled with potass, furnishes another compound of ethyle and ammonia, of the formula $NH,2C_4H_5$, or biethylamine, which, like ethylamine, has the basic properties of ammonia; by a similar process with this body, a triethyle compound with azote is formed, and finally, by the action of iodide of ethyle on this body, a compound of iodide of ethyle and triethylamine is formed; and by the action of salts of silver, on this iodine being separated, there remains a hydrated oxide of tetrethyle-ammonium, of the formula $N4(C_4H_5)O,HO$.

METHYLAMINE, $C_2H_3,H_2N$, Amide of Methyle, is obtained by decomposing the cyanate of methyle with alkalies. The cyanate of methyle is produced by passing cyanic acid into wood spirit. The cyanate of methyle is then to be distilled with potass. Methylamine is a gas which must be collected over mercury, like ammonia; or an aqueous solution of it may be formed saturated with hydrochloric acid, and a muriate of methylamine obtained by evaporation and crystallisation, which will yield methylamine when distilled with lime, precisely like muriate of ammonia. It may likewise be obtained by the action of ammonia on iodide of methyle. Methylamine has an ammoniacal smell resembling also that of putrid fish; it has an alkaline reaction. It is a liquid at 32°, and is then heavier than water. It is absorbable by water to the extent of 1,150 vols., at $55\frac{1}{2}$°. It is so generally like ammonia, that but for its inflammability, it could hardly be distinguished from it; and probably it is often, when a product of various organic decompositions, confounded with it. Its solution precipitates metallic salts as ammonia does, and it re-dissolves precipitated oxide of copper, giving a fine blue coloured solution. With the salts of silver it forms a black precipitate similar to fulminating silver, but which is not explosive. Methylamine neutralises acids, and forms compounds analogous to those of ammonia, and the bichloride of platinum and mercury and terchloride of gold form double salts with the chloride of methylamine, as with ammonia. This chloride is obtained by saturating methylamine with muriatic acid gas, or boiling cyanate of methyle and potassa, decomposing by hydrochloric acid and evaporating to crystallisation. It is a colourless salt, which crystallises in plates, melts at the boiling point of water, and may be sublimed.

*Dimethylamine* and *Trimethylamine* are formed in the action of iodide of methyle on ammonia. There is also a hydrated oxide of tetramethyl-ammonium.

*Amyle* compounds, similar to those of ethyle and methyle of this class, exist.

ANILINE, $C_{12}H_7N$, Carbolic Acid, has been spoken of as the hydrate of the oxide of phenole, or $C_{12}H_5O,HO$. The present compound cannot be prepared like ethylamine or methylamine. When carbolic acid, however, is treated with ammonia in sealed tubes, aniline is produced. It is formed in a great many cases. Indigo and isatine, under the influence of potass, disengage hydrogen and give origin to aniline. It is best obtained by dissolving indigo blue, with the aid of heat, in a hot concentrated solution of potassa, then drying the mass and distilling it. It must be separated from an ammoniacal liquid which accompanies it, and redistilled. It is also obtained by neutralising and agitating oil of tar with the strongest commercial muriatic acid, and then leaving them together for some hours; the liquid then separates into two layers, of which the upper contains the oil deprived of its alkaline principles. The inferior acid layer is to be shaken with a fresh quantity of oil of tar, and, when the hydrochloric acid is saturated, it is mixed with a quantity of milk of lime in excess and distilled; at first a milky liquid is distilled, containing a mixture of aniline and quinoline (leukol); these bases are saturated with hydrochloric acid, ether is then added, which takes up the non-alkaline oils, while the alkaloid salts rest in a layer beneath the ether. The two organic bases are displaced by potass, and aniline obtained by distillation at 360°. It may be obtained by several other processes. It is a limpid oily fluid, possessed of an agreeable odour, and of an aromatic burning taste. It is liquid at 4°. It boils at 360°, and burns with a brilliant smoky flame. Sp. gr. 1·042. It is slightly soluble in water, and in all proportions in alcohol, wood spirit, acetone, &c. At a high temperature it dissolves phosphorus and sulphur. It does not affect litmus or turmerie. It gives a white cloud, with vapours of hydrochloric acid. Chloride of lime produces a violet colour with aniline and its salts, which does not remain; chromic acid, a green, blue, or black precipitate, according to the concentration of the aniline. When concentrated hydrochloric acid is introduced into an alcoholic solution of aniline, and some crystals of chlorate of potass are added, chloranile is produced, $C_{12}Cl_4O_4$. Chlorine, bromine, and iodine form compounds with aniline, in which 3 equivalents of hydrogen are removed, and 3 of the halogenous element substituted. Aniline precipitates several metallic oxides from solutions of their salts, but not the nitrates of mercury and zinc. It combines with the chlorides of mercury, platinum, palladium, and gold. Aniline forms a remarkable series of salts, colourless, but which assume a rose colour when exposed to the air, crystallisable and well-defined, containing generally 1 atom of base and 1 of acid,—such are the sulphate, oxalate, muriate, &c.; and, by distillation of several of their other compounds, compounds are

formed bearing the same relation to them that oxamide, sulphamide, &c., bear to the analogous compounds of ammonia ; for example, the oxalate of aniline, on being heated, yields oxanilide,—that is to say, $C_2O_3,HO,C_{12}H_7N$, becomes $C_2O_2,C_{12}H_6N$. Nitraniline contains the elements of aniline with 1 eq. of hydrogen removed and 1 of hyponitrous acid substituted for it. *Trilaniline*, $C_{26}H_{13}N_3$, is formed by the action of dry chloride of cyanogen and anhydrous aniline; the chloride of melaniline is then formed, and when mixed with water an oil is separated, which solidifies into a yellow crystalline mass— this is melaniline. Chlorine, bromine, iodine, and nitric acid furnish compounds with melaniline, in which 2 eqts. of hydrogen are removed and 2 of the agent substituted. With cyanic acid aniline forms a compound analogous to urea.

*Picoline* is a principle isomeric with aniline found in the first parts of the products of the distillation of oil of tar. Among other points in which it differs from aniline is, the absence of the reaction mentioned with chloride of lime.

*Kinone, Quinone*, $C_{25}H_8O_8$. When kinic acid or a quinate is decomposed by heat, numerous compounds are formed belonging to the benzoic or salicylic series, except one, which is the most abundant of all, known as colourless hydrokinone, $C_{12}H_6O_4$. The same kinic acid, subjected to distillation with sulphuric acid and peroxide of manganese, gives a volatile product known as quinone. If this is compared with the hydrate of the oxide of phenyle, $C_{12}H_8O_2$, it is then seen that it only differs from it by the substitution of two equivalents of oxygen for two of hydrogen.

*Kinone* is obtained by mixing one part of kinic acid, four parts of peroxide of manganese, and one of sulphuric acid, diluted with half its weight of water. A violent effervescence takes place; the products of the reaction are subjected to cold, and there condenses a mixture of formic acid and kinone. The latter crystallises in splendid gold-coloured plates. The kinone is then to be expressed, dried over chloride of calcium, and sublimed. This body has a great tendency to crystallise like camphor ; it has a strong and irritable odour ; heat melts it and causes it to sublime in long crystals. It is heavier than water; melts and partially dissolves in boiling water ; soluble in alcohol and ether. Chlorine acts powerfully upon it, giving rise to a sesquichloride, as it is termed, $C_{24}H_2Cl_6O_8$.

*Chloranile, or the Perchloride of Kinone*, $C_{24}Cl_8O_8$, is formed from several organic substances ; kinone yields it abundantly, as well as salicine. The best way to form it is to act upon the organic substance with hydrochloric acid, and chlorate of potass ; the liquor becomes yellow, and crystals of chloranile form ; these are washed with water, and dissolved in boiling alcohol. It is insoluble in water, and nearly so in cold alcohol. Potass forms with it an acid, the chloranilic, ammonia chloranilam. Muriatic and other acids combine with it, forming salts.

*Hydrokinone, Hydroquinone*, $C_{24}H_{12}O_8$, is formed by directing a current of sulphurous acid into a solution of kinone containing also.

kinone suspended. The current is continued until a colourless liquid is obtained. On concentrating, crystals of hydrokinone are deposited; sulphuric acid is to be removed by carbonate of baryta. It crystallises in hexagonal forms, has a sweet taste, without smell, soluble in water and alcohol; is sublimable; but by a too strong heat is decomposed into yellow and green kinone. The latter body has the composition $C_{24}H_{10}O_{8}$, and is obtained by the action of oxidating agents on hydrokinone, or of reducing agents on kinone; thus, per-chloride of iron and bichromate of potass oxidate hydrokinone, and platinum black and animal charcoal, moistened with solution of hydro-kinone, change it into the green kinone. It forms splendid feathery crystals; green by reflected, red by transmitted light; soluble in alcohol and ether; slightly so in water. Is fusible by heat, and sub-limes in green plates,

Among these bases must be enumerated the substance known as *Naphthalidame* or *Naphthalidine*, $C_{20}H_{9}N$, or $C_{20}H_{7}NH_{2}$, which is a very strong base. It is prepared by the reaction of sulphuretted hydrogen on an alcoholic solution of the protonitrate of naphthaline; one part of the protonitrate is added to ten parts of very strong alcohol; the liquid is saturated with ammonia, and a current of sul-phuretted hydrogen passed through. All the protonitrate dissolves, and the liquid becomes of a green colour. It is left alone for some time; sulphur is deposited; the alcohol is driven off; and the liquid is decanted and distilled as long as sulphur is deposited. The con-centration is then pushed until the liquid separates into two layers, of which the lower becomes a mass of solid naphthalidame. To obtain it pure, it is dissolved in dilute sulphuric acid, the sulphate is several times crystalised, and the naphthalidame precipitated by caustic ammonia. Thus obtained, it is in fine white milky needles; melts at 86°; boils at 572°; subliming without alteration. It is almost insoluble in water, but very soluble in alcohol and ether. It has no alkaline reaction with vegetable colours, but forms salts with acids.

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# CHAP. 8.—ORGANIC ACIDS AND BASES.

MANY of these substances have been already described. Others can with difficulty be brought into any other class; and many pos-sess such well-defined acid or basic qualities, as to cause them to stand out from most of the other bodies hitherto described as con-spicuous representatives of their respective classes. For instance, oxalic or tartaric acid is a very different substance, as far as acid properties are concerned, from mucic or uric acid; and in the same way morphia, or quina, is a very different substance from urea. This

chapter may be conveniently divided into sections: 1st, organic acids; 2nd, organic bases.

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<div align="center">SECT. I.—ORGANIC ACIDS.</div>

It is exceedingly difficult to classify these; such as could be attached very distinctly to different groups have already been spoken of. The best division appears to be the following; but it is too elaborate to be followed out in this work, where only the principal substances can be spoken of    1st. Those acids which are formed by the oxidation of carbon, when the chief elements are some compound of carbon and oxygen with water; such are the carbonic acid, $CO_2$, the oxalic acid, $C_2O_3,HO$, the meconic, $C_{14}O_{10},10HO$.    2nd. Acids formed by the oxidation of a hydrocarburet. These would be a very long list, including the fat acids, as has been already pointed out; such acids as formic acid $(C_2H)O_3$ could also be included. 3rd. Acids formed by the union of carbonic acid with other organic groupings; a very great number of acids could be put under this head, otherwise ranked far apart,—for instance, oleic acid, $C_{34}H_{34},C_2O_4$, salicylic acid, $C_{12}H_6O_2,C_2O_4$, and mucic acid, $C_9H_{10}O_{10},CO_2$. 4th. Acids formed by the intimate union of other acids. Many acids might be ranked under this head, as indeed it is not difficult, with a little ingenuity, to split the complicated formulas of several of the organic acids into more than one or two formulas of other acids, from whose direct union, however, the more compound bodies cannot themselves be formed; any more than many of the organic compounds themselves which have radicals assigned them, can be formed from the direct action of the compound radicals and the other elements. Thus tartaric acid, $C_8H_6O_{12}=C_4H_4O_4+2(C_2O_3,HO)$, or one equivalent of acetic acid and two of oxalic. 5th. Acids represented by a hydrate of carbon, as lactic acid, $C_6H_6O_6$, humic, $C_{40}H_{15}O_{15}$, or $C_{40}H_{12}O_{12}$. Then there are acids formed by the intimate union of a hydrocarburet with some of the preceding acids. But the acids treated of will simply be taken in the following order:—

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|---|---|
| Oxalic | Tartaric |
| Formic | Citric |
| Tannic | Malic |
| Gallic | Aspartic |
| Meconic | Kinic |

And some peculiar animal acids in speaking of the composition of the animal fluids.

OXALIC ACID, $C_2O_3HO+HO$. Eq. $36.9+18$. Oxalic acid is prepared by several processes. The most usual is to treat 1 of sugar or starch with 5 of nitric acid of sp. gr. 1·42 diluted with 2 of water, using a gentle heat until fumes cease to be evolved. The solution is

then concentrated, and on cooling affords copious crystals of oxalic acid. These are to be drained either on a dry tile or by paper, and again dissolved in water and recrystallised. It may also be prepared by decomposing the binoxalate of potass with acetate of lead when oxalate of lead is thrown down, which may be decomposed while still moist with sulphuric acid, when oxalic acid is set free, and may be removed by solution and filtration.

Oxalic acid crystallises in irregular six-sided prisms. They contain 3 eqts. of water, of which they lose 2 when heated a little above 212°; when the hydrate heated above this point sublimes in flocculi. At a higher temperature, at 311°, oxalic acid is resolved into formic acid, and carbonic acid, and carbonic oxide. Many oxidating substances convert oxalic acid into carbonic acid, and the agency of peroxide of manganese in this way has been applied as a test of the purity of the manganese. For this purpose muriatic acid, manganese, and oxalic acid are heated together, a chloride of calcium tube having been fitted to the apparatus, and the whole weighed, the loss of weight from disengagement of carbonic acid will then indicate the purity of the manganese. Oxalic acid crystals dissolve in 8 parts of water at 60°, in twice their weight of water at 212°, and in 4 parts of alcohol. Oxalic acid should dissolve in water without residuum; precipitate soluble salts of lime, giving a precipitate which first becomes black, then white, when heated in a platinum crucible, and a white precipitate with nitrate of silver, which when dried on the filter, and gently heated upon it, goes off with a kind of rapid effervescence or feeble explosion. Most of the oxalates are readily prepared by the addition of oxalic acid to bases or their weak salts, or by double decomposition of their soluble salts by alkaline oxalates. They are a well characterised class of salts. It need hardly be remarked that oxalic acid is a powerful acid, and a corrosive and irritant poison. The best antidote to it is chalk or magnesia. In testing for it in organic mixtures, the best mode is to obtain as clear a solution as possible and precipitate it with acetate of lead, decomposing the oxalate of lead with sulphuretted hydrogen, or if lime or magnesia has been given, boiling with carbonate of potass so as to reform a soluble oxalate, which can then be precipitated with sulphuretted hydrogen.

FORMIC ACID, $C_2HO_3,HO$, is derived from wood spirit, as acetic acid from alcohol, viz., by the substitution of two eqts. of oxygen for two of hydrogen; thus $C_2H_3O-(H_2+O_2)=C_2HO_3$. It may be obtained by expression or distillation from red ants. It is usually prepared by mixing together one part of starch with four of sulphuric acid and four of water; and after heating and allowing the mixture to cool, then adding four parts of the peroxide of manganese and distilling. The formic acid which comes over is at first very impure, but by the addition of carbonate of soda, the formiate of soda may be obtained and crystallised, and this decomposed by dilute sulphuric acid, and a purer formic acid obtained by distillation. The removal of hydrogen from starch or grape sugar, and the addition of oxygen by the action

of peroxide of manganese, and $SO_3$, will explain the formation of formic acid in this process. Formic acid may be obtained by other processes. It closely resembles acetic acid, from which it is distinguished by its action with oxide of silver, or mercury in solution. It reduces the metals. It is a colourless fluid of sp. gr. 1·235, soluble in water in all proportions; heated with alcohol it forms formic ether. It boils at 209°; cooled to 32°, it crystallises in brilliant plates. It is very inflammable. Its salts, called formiates, are most soluble and crystallisable.

TANNIC ACID, $C_{18}H_5O_9$, $3HO$, *Tannine, Quercitannic Acid.* This acid is the type of a whole series of astringent substances which exist in different plants, of which it is the most important. The differences between these principles is not yet well known, and as they do not crystallise, the means of obtaining them pure are to a great extent wanting. Such differences exist, as that the tannine of bark, tea leaves, the infusions of kino and catechu precipitate persalts of iron green, while ordinary tannine gives the fine bluish black colour known as the basis of ink.

Tannine exists in many plants. It is best obtained from powdered nut-galls. For this purpose, an ethereal solution of galls is prepared in the mode termed displacement; that is to say, a long narrow funnel has its mouth loosely stopped by cotton. Above this is placed the powdered galls to the extent of half the capacity of the long funnel. It is then loosely stopped, and placed in a flask, and the ether poured in upon the powder. Next day will be found in the flask, a liquid divided into two layers, a light one at the top; a heavier, coloured amber, and like syrup, at the bottom. The treatment by ether is renewed as long as the denser fluid which contains the tannine is formed. The upper fluid contains the gallic acid and other substances. The heavy fluid is evaporated over sulphuric acid *in vacuo.* Tannine thus obtained is a light spongy yellowish mass, which reddens litmus, and has an astringent taste. It is soluble in water, the solution reddens litmus, and effervesces with the alkaline carbonates; is precipitated by several mineral acids, and gives precipitates with many inorganic and organic substances. Of the latter may be mentioned the salts of cinchonina, quina, brucia, strychnia, codeia, narcotine, and morphia. All these precipitates are soluble in acetic acid and alcohol. Acetate of lead precipitates the tannate of lead from the alcoholic solution, and the alkaloid combines with the acetic acid, and remains in solution. With a solution of gelatine, tannine throws down a white opaque precipitate, soluble if the tannine be not in excess in the supernatant liquid by the aid of heat, but if the tannine be in excess it is insoluble by the aid of heat; and forms an elastic grayish membrane. Tannine also precipitates the solutions of starch, vegetable and animal albumen, and gluten. All the animal solids absorb it from its aqueous solution. In tanning, the skin of animals absorbs it, and becomes the substance known as leather. In contact with oxygen, a solution of tannine absorbs it, carbonic acid is evolved, and crystals of gallic

acid formed. Tannine inflamed in contact with air, burns without residuum. Its watery solution is precipitated by the mineral acids, and compounds with tannine and the acid used are formed.

GALLIC ACID, $C_7HO_{32},HO$, is best obtained by precipitating the tannine from infusion of nut-galls by gelatine, evaporating the residual liquor to an extract; heating the extract with boiling alcohol, and evaporating the alcoholic solution to an extract; treating the alcoholic extract with ether, and crystallising the gallic acid from the ethereal solution, decolourising by animal charcoal. There are several other processes by which it may be prepared. It crystallises in fine grayish silky needles, soluble in 100 parts of cold water, in 3 parts of boiling water, very soluble in alcohol, and less so in ether. The chief difference between it and tannic acid is, that it does not precipitate gelatine, and that it is not absorbed by the animal tissues as tannine is. When heated strongly it is resolved into carbonic acid, water, and an acid which remains in the retort as a black shining mass, metagallic acid. This takes place about 480°. At 420° carbonic acid is given off, and a new acid sublimes in brilliant white plates; this is the pyrogallic acid. A solution of nut-galls long exposed to the air leaves crystals of gallic acid. It gives a bluish black precipitate with persalts of iron.

MECONIC ACID *and its products*, $C_{14}HO_{11},3HO,6HO$. Meconic acid is prepared from meconate of lime, produced in the preparation of morphia. This is dissolved in 20 parts of water and 3 of muriatic acid at near the boiling point, and on cooling, a supermeconate of lime is deposited in the form of crystals. These are drained on a cloth, and then squeezed. The process of solution in the muriatic acid and water, is repeated until the lime is deprived of all its meconic acid, which crystallises nearly pure. It is difficultly deprived of its colour, but this may be done by forming a meconate of potass and decomposing this in solution by muriatic acid. Meconic acid crystallises generally in white pearly plates, which are not very soluble in cold water, but very soluble in boiling water. The crystals at 212° lose 6 eqs. of water. It has a sharp astringent taste, and acid reaction. It is recognised by its remarkable power of striking a deep red tint with persalts of iron, the meconate of iron. This colour is similar to that afforded with the same salts and compounds of sulphocyanogen; but in the latter case, solution of corrosive sublimate removes the colour, which it does not do in the former. Meconic acid is combustible, and leaves no residue. At a temperature of 248°, meconic acid begins to be decomposed, and yields water, carbonic acid, and a residue of *comenic* acid, mixed with a small quantity of an insoluble gray or brown matter. Heated from 511° to 550°, pyromeconic acid is formed, and an acid isomeric with the *comenic* acid, the *paracomenic*.

Meconic acid is best detected in the contents of the stomach, by adding water, boiling, precipitating the meconate of lead by sugar of lead, and decomposing this, diffused in water, with sulphuretted hydrogen. The solution must be concentrated, and the sulphuretted

hydrogen completely driven off, and a persalt of iron then added. Chelidonic acid, very similar to comenic, has been obtained from the *chelidonium magus.*

TARTARIC ACID, $C_8H_6O_{12}$, or $C_8H_4O_{10}$,2HO, *and its derivatives.* Tartaric acid is easily prepared by dissolving cream of tartar, and bitartrate of potass in boiling water, and adding chalk to the solution as long as there is effervescence. An insoluble tartrate of lime is formed, and tartrate of potass remains in solution. The precipitate is removed, and the solution treated with chloride of calcium; double decomposition ensues, chloride of potassium remains in solution, and more tartrate of lime is formed. The whole tartrate of lime, after being washed, is decomposed by digesting with dilute sulphuric acid. The solution of tartaric acid is then evaporated and crystallised. Tartaric acid crystallises in oblique prisms, with a rhomboidal base, or in hexagonal prisms. These crystals have a sp. gr. of 1·75. Tartaric acid melts at above 400°, and loses 2 eqts. of water. It is then insoluble in cold water, but dissolved in boiling water, it reconstitutes the original acid. It passes in this through two modifications, becoming *tartralic acid*, $C_{12}H_6O_5$,HO, and *tartrelic acid*, $C_8H_4O_{10}$HO, and finally the anhydrous acid, $C_8H_4O_{10}$. The two first are soluble in cold water. The acid properties of tartaric acid are well known.

When tartaric acid is distilled, a heavy oily acid substance passes; carbonic acid, acetic acid, and other products of the destructive distillation of organic substances pass. The distilled fluid contains an acid of the formula $C_5H_3O_3$,HO which crystallises on evaporation of the fluid in long prisms. It is a very characteristic acid, and does not, like tartaric acid, give a precipitate with lime water.

*Racemic Acid, Paratartaric Acid,* $C_4H_2O_5$HO. This acid closely resembles the tartaric acid. It accompanies it in the grapes of upper Rhine. On decomposing the tartrate of lime by sulphuric acid, the racemic acid crystallises first. It differs in chemical properties from tartaric acid, chiefly in precipitating nitrate, muriate, and even sulphate of lime in solution. By the action of heat it yields paratartaric, *paratartralic*, and *paratartrelic* acids, which last are obtained by the action of heat on tartralic and tartrelic acids.

CITRIC ACID, $C_{12}H_5O_{11}$,3HO. Tartaric acid exists chiefly in grapes, although in other fruits and vegetables; citric acid in oranges, citrons, and gooseberries, also in strawberries, raspberries, and other vegetables. It is obtained by neutralising lemon-juice with chalk, and decomposing the citrate of lime by means of sulphuric acid, when citric acid remains in solution, and can be obtained by evaporation and crystallisation. It crystallises in rhombic prisms, with octohedral summits. These crystals have an acid, pleasant taste. The crystals lose 2 eqts. of water at 212°. Citric acid is soluble in water, in alcohol, and very slightly so in ether. When citric acid is heated, a gas is disengaged which condenses in oily layers on the neck of the retort. In the retort, after a time, the citric acid will be found to be replaced by another acid, the *aconitic*, which is very

soluble in ether, unlike citric. It is a white crystalline mass, soluble in water and alcohol, and possessed of decided acid properties. It exists in monkshood, under the form of aconitate of lime, and in the equisitum fluviatile as aconitate of magnesia. When aconitic acid is heated it gives rise to two new acids, the *citraconic* and *itraconic*.

MALIC ACID, $C_8H_4O_8$,HO (Sorbic Acid), exists principally in apples and pears, and other vegetables. It may be obtained by bruising nearly ripe berries of the mountain ash or rowan, and nearly saturating the juice with milk of lime, then boiling for some hours; a crystalline crust of malate of lime forms, which is to be removed, and well washed with cold water, then dissolved with the aid of heat, in water containing a tenth of nitric acid; it is then filtered, and the acid malate of lime is precipitated. This is repeatedly crystallised, and then decomposed in solution by acetate of lead, and then malate of lead by sulphuretted hydrogen. The solution on evaporation gives confusedly crystalline deliquescent crusts. Malic acid can be obtained from tobacco, and in large quantity from rhubarb. It is very soluble in water, and in alcohol. When heated it undergoes the watery fusion, and at 349 it is converted into *maleic* and *paramaleic* acids. The latter is formed when maleic acid is kept continuously heated for some time. The formula of maleic acid is $C_8H_2O_6$,2HO, and that of paramaleic or fumaric acid $C_4HO_3$,HO; hence its formation from maleic acid, and that of both from malic, by heat is obvious enough. The most characteristic of the salts of malic acid is the malate of lead, which separates from a hot solution in a dilute acid, in beautiful silvery crystals.

ASPARTIC ACID, $C_8NH_7O_8$, *and Asparagine*, $C_8N_2H_{10}O_8$. Asparagine may be obtained by evaporating the expressed juice of vetches, asparagus, and other plants which contain it, and especially of the marsh-mallow. The best way is to macerate the cut and bruised marsh-mallow roots with milk of lime; precipitating the fluid with carbonate of ammonia, and evaporating the remaining fluid to a syrup; brilliant crystals form. When a current of nitrous gas is passed into a solution of asparagine or aspartic acid, nitrogen is eliminated, and malic acid formed by the liberation of water, as may easily be understood by comparing the formula of these substances with that of malic acid. Aspartic acid is also formed by boiling asparagine with barytic water as long as ammonia is evolved, and precipitating the barytes by sulphuric acid. The aspartic acid may then be crystallised. Fumaric acid, whose formula has already been given, may be obtained either from fumitory or Iceland lichen. From the latter by digesting it for several days with milk of lime, expressing the liquid, then acidulating with acetic acid, adding the basic acetate of lead as long as a coloured precipitate is produced, and when this becomes white, filtering the liquid boiling. The fumarate of lead crystallises on cooling, and is to be decomposed by sulphuretted hydrogen. Fumaric acid crystallises in fine, brilliant, colourless needles, of an acid taste, soluble in hot water and alcohol.

KINIC ACID, $C_{11}H_{12}O_{12}$, or $C_{14}H_{11}O_{11}$,HO, exists in Peruvian bark

as kinate of quina ; and is separated in the process for preparing that
alkaloid.    When the bark is boiled with hydrochloric or sulphuric
acid, and the extract precipitated by milk of lime in excess, the fil-
tered liquid contains the kinate of lime, which crystallises by evapo-
rating to a syrup, and can be purified by animal charcoal and repeated
crystallisations.    The kinic acid may be separated by heating gently
the kinate of lime with one part of sulphuric acid and ten of water ;
sulphate of lime is precipitated, and, the supernatant liquid being
removed and alcohol added, is gently evaporated to a syrupy consis-
tence.    After a time kinic acid crystallises in transparent prisms.
Kinic acid is soluble in $2\frac{1}{2}$ parts of boiling water, and is very soluble
in dilute alcohol.    Distilled with sulphuric acid and peroxide of
manganese it yields yellow plates of kinone, and when these are
treated with sulphuric acid, white and green hydrokinone are
formed.

Many other organic acids exist besides those specified, and many
others have been described or alluded to under other heads.

## SECT. II.—ORGANIC ALKALIES.

These substances so far justify their title in being the antagonistic
substances to the organic acids.  They have been considered primitive
groupings analogous to ammonia, uniting to water and forming bases,
and then becoming distinctly alkaline and forming salts ; and as am-
monia was observed to form compounds with organic bases, in which
the ammonia as such was dispensed with, so it is the same with the
body supposed with the water to constitute the organic base with
the alkaloids,—thus we have morpho-metallic, quino-metallic oxides.
Since the first discovery of the organic alkalies, their field of obser-
vation has been materially extended, especially of late.    They are
not merely substances found in plants, but in the animal tissues, the
dry distillation of organic fossils, and animal products.    Essential
oil of mustard yields several ; opium a great number ; and reference
to the organic bases of artificial origin, especially aniline, will show
the numerous sources from which these substances can be obtained.
Some of the modes of proceeding have become almost recipes for the
formation of an alkali ; for instance, the action of hydrosulphate of
ammonia upon the nitrogenised products of some of the principal
organic series.    All these principles contain azote, which seems a
necessary condition of their production, and all hydrogen and carbon;
most also contain oxygen.    In the principles derived from essence of
mustard, sulphur and selenium are also found.    They are generally
solid, sometimes liquid, especially where oxygen and sulphur are
wanting.    They are colourless or yellowish, generally of a bitter and
acrid taste ; they are slightly soluble in water, more so in alcohol,
sometimes in ether.    When not volatile, they are decomposed by heat,
giving fetid products and yielding a black residue.    They burn

easily on account of the quantity of carbon which they contain. The other properties of these bodies will be best learned from their individual history.

They may be divided into the following groups :—1st. Those which are liquid and volatile. 2nd. Those which are solid, obtained from plants. 3rd. Those of animal origin.

## I.—*Volatile non-Oxygenated Alkaloids.*

*Leucoline*, $C_{18}H_7N$.* After having taken the proper precautions to extract aniline from oil of tar, leucoline is obtained in the latter stages of the operation. The oils which then pass over are shaken with strong muriatic acid, and distilled with milk of lime in a copper still. The distilled fluid is treated with muriatic acid again, and evaporated; then distilled again, and only those portions which come over last, and when the heat is up to 460° retained. It can also be prepared by heating several alkaloids, as quina and strychnia, with potassa, and distilling. It is colourless, acrid, and with a disagreeable smell; sp. gr. 1·081. It is inflammable, becomes brown and resin-like in air; nearly soluble in water, soluble in alcohol and ether. Boils at 462°, dissolves sulphur, phosphorus, and camphor; is soluble in acids, with which it forms crystalline salts.

CONEIA, *Coneine, Conicine, Cicutine,* $C_{16}H_{16}N$, is obtained from the leaves and stalk of the hemlock. These bruised are to be distilled with potass lye. Ammonia is formed at the same time, which condenses with the coneine; the whole is saturated with sulphuric acid, and evaporated to a syrupy consistence, then exhausted by a mixture of alcohol and ether, which does not dissolve the sulphate of ammonia, but dissolves the sulphate of coneia. This last salt is anew decomposed by caustic potass. The coneine is dried by digestion over chloride of calcium, decanted and distilled. It is a pure oily colourless substance, of an acrid and disagreeable smell, and very poisonous; sp. gr. 0·89, boils at 338°. It quickly browns when exposed to the air, slightly soluble in water, soluble in all proportions in alcohol, ether, essences, and fat oils. It is very alkaline, and precipitates the salts of mercury and persalts of iron, salts of copper and silver. Hydrochloric acid gas colours it of a deep purple, and the liquid acid produces a white transparent and deliquescent muriate, which heated, becomes purple. Nitric acid colours it red, and sulphuric acid forms a purple compound with it, which soon becomes green.

NICOTINA, *Nicotine,* $C_{10}H_7N$, is prepared by forming, in the first place, watery extract of tobacco of the consistence of a syrup, which is treated while hot with twice its volume of alcohol. Two layers separate, of which the upper contains the nicotine. This is decanted, and the alcohol driven off. The residue is then treated with a strong solution of potass; when the mixture is cold, it is then treated with ether, and to

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* Called also quinoleine and leucol.

the decanted ethereal solution oxalic acid in powder is added. Oxalate of nicotina assembles in drops; these are washed several times with ether, decomposed by potass, taken up again by ether, and the ether distilled off by the water bath; at last the remainder is exposed to a current of dry hydrogen at 284° for several days, and finally distilled at 356°. Nicotine is an oily limpid liquid, with a feeble smell of tobacco, which boils at 585°, and decomposes at that point. Its sp. gr. is 1·048, and it is inflammable. It is powerfully alkaline. It is slightly soluble in water, but the addition of caustic potass precipitates it in drops. Ether dissolves it in all proportions. It is also soluble in the oils and essences. It becomes brown and resinoid in the air. It is very poisonous. Its salts with sulphuric and nitric acid are deliquescent. The weaker acids are all neutralisable by nicotina; exposed to the air they become coloured, red, violet, then green, or of a deep blue.

## II.—Solid Alkaloids from Plants.

The various species of cinchona barks employed in medicine contain two principal alkaloids, quina and cinchonina; but they also contain, or are supposed to contain, other principles of the same character, *quinidine, cinchonidine*, and *cinchovatine* identical with aricine, and also other principles little known.

QUINA, *Quinine*, $C_{20}H_{12}NO_2$, or $C_{38}H_{22}N_2O_4$, symbol Qu. There is some doubt about the composition of this substance; we shall take the latter formula as the more recent. It is easily prepared from the ordinary disulphate, by dissolving it in water acidulated by sulphuric acid and precipitating by ammonia. The mixture should be heated to the boiling point, and the precipitate well washed. It is a white flocculent substance of an intensely bitter taste, soluble in 200 parts of hot water and in alcohol. It crystallises from a hot alcoholic solution by the addition of ammonia in silky crystals. When heated it melts, and is partly volatilised, partly decomposed. Ether dissolves it, and thus affords a means of separating it from cinchonina, which is not thus soluble. The best test for quina is to dissolve it in water acidulated with hydrochloric or sulphuric acid, then pouring in a solution of chlorine water, and adding in the last place liquid ammonia. The solution takes a fine green colour, and then, if treated with an acid, becomes a deep red.

*Sulphates of Quina, Disulphate of*, $2(C_{38}H_{22}N_2O_4)SO_3HO$, or $Qu_2SO_3HO$. Among the infinite variety of species of bark are three kinds which are classed as generic, yellow, red, or gray barks. The gray contains the most cinchonine, the red barks contain about equal quantities of the two alkaloids, the yellow barks contain most quina, and from them principally is the quina prepared. The bark is first finely bruised, then boiled with 8 or 10 parts of water, containing 12 per cent. of sulphuric or 25 per cent. of muriatic acid.

The boiling is continued for an hour; then the decoction filtered through cloth, and more water is then boiled with the residual bark as long as it gets a bitter taste. Into the cooled decoction milk of lime is put until the liquor becomes alkaline. The precipitate formed is strongly pressed, and when dry is treated with boiling alcohol, sp. gr. 0·847, as long as the alcohol takes up anything bitter. Three-fourths of the alcohol are separated by distillation, and the residue is rendered acid by the addition of sulphuric acid. The sulphate is purified by boiling with animal charcoal and repeated crystallisation.

Disulphate of quina crystallises in white feathery crystals. The salt of quina crystallises first from the solution, leaving the sulphate of cinchonina. It requires 740 parts of cold water to dissolve it, but is soluble in 30 parts of boiling water and 80 of alcohol (0·850).

*The Sulphate of Quina,* $QuSO_38HO$ (neutral sulphate), is prepared by dissolving the disulphate in dilute sulphuric acid, evaporating. It crystallises in rectangular prisms. It is soluble in about 11 parts of cold water, and in its water of crystallisation at 212°. It is also soluble in alcohol.

*Adulterations* of sulphate of quina are often practised. There is great temptation to adulterate it with the sulphate, as the latter loses 24 per cent of its water of crystallisation if long heated at 212°; and, moreover, contains a large quantity of additional $SO_3$. Besides, this sulphate of quina of commerce is adulterated with many other substances. The cinchonina will be found by precipitating a solution of both salts by ammonia, and treating the precipitate by ether, which dissolves the quina and leaves the cinchonina. At 248° the cinchonina does not lose weight, whereas quina loses 14·2 per cent. The salt should be crystallised in needles or prisms; no amorphous masses should be present which among other things would indicate quinoidine. The salt should be burnt without residue in a platinum capsule, which would not be the case if it contained inorganic matter. If salicine be present, it would give a red colour with oil of vitriol; boracic acid sometimes used would give a green colour to the flame of an alcoholic solution, and sugar may be detected by fermentation. *Quinoidine* is isomeric with quina. It is amorphous. It appears to be produced in the manufacture of quina in a way not well understood. It is doubtful how far it possesses the medicinal virtues of quina. *Quinidine* has been found existing with quina in some of the new barks. It too is isomeric with quina, but its salts are efflorescent. *Quinicine* is produced by exposing sulphate of quina moistened with sulphuric acid and water to a temperature between 248° and 266° for a few hours. It then begins to resemble cinchonina more than quina.

*Cinchonina,* $C_{38}H_{22}N_2O_2$, or $C_{20}H_{12}NO$; Ci; is obtained from gray bark, in the same way as quina is produced from the yellow bark, but it can be obtained from the mother waters which remain after the preparation of sulphate of quina. If quina and cinchonina be precipitated together, the quina may be separated by hot alcohol, which

lets the cinchonina crystallise on evaporation, but retains the quina. Its crystals are four-sided prisms. It melts at 329°, and may be sublimed. Its taste is much less bitter than that of quina. It is much less soluble than quina in water, alcohol, and ether. The salts, on the other hand, are more soluble than those of quina, and are not precipitated by the salts of silver, which precipitate those of quina.

Both cinchonina and quina yield leucoline when heated with potass. *Cinchonadine* (cinchonidina) is isomeric with cinchonine; exists in commercial quina; *cinchovatine (cinchovatina)* is extracted from cinchona ovata. It is insoluble in water, melts about 360° and upwards, and is decomposed into fœtid gases.

### ALKALIES OF OPIUM.

No vegetable production contains such a prodigious number of organic principles as opium. It contains morphia, codeia, narceia, narcotina, opianina, papaverina, porphyroxina, pseudomorphina, thebaina, meconic acid, various extractive and fatty matters, volatile oils, a substance like caoutchouc, lignine, pectic acid, and salts. It is not certain, however, that all these can be found in all the specimens of opium. Morphina and narcotina are the most abundant.

NARCOTINA, *Narcotine*, $C_{46}H_{25}NO_{14}$, is obtained by exhausting opium with ether. Narcotina, morphia, and porphyroxina are removed. When the ether is driven off, water removes the morphia. The residue is to be dissolved in alcohol and potass added, the narcotina and porphyroxina are then precipitated. They are to be dissolved in muriatic acid, and the solution concentrated; the muriate of narcotine is the first to precipitate, and the mother water contains the muriate of porphyroxina. This base may be precipitated by ammonia in excess, and the precipitate being dissolved in boiling alcohol, on evaporation the porphyroxina is deposited in brilliant colourless needles. The narcotina may be obtained by precipitating it from the muriate, and crystallising it from boiling alcohol; but it remains undissolved when opium is exhausted by water, and may be taken up from the residue by ether. Narcotina crystallises in straight prisms with a rhomboidal base, or in needles. It melts at 338°, and about 429° it loses ammonia, and becomes a brown friable mass which has been called humopic acid, and contains no azote. It is insoluble in cold water, requires 500 parts of hot water; alcohol dissolves about 5 per cent., and ether 2 per cent. of it. Although it forms salts with acids, its solutions are not alkaline. It is soluble in essential and fatty oils, and in that form its narcotic powers are much augmented. It is coloured red by concentrated sulphuric acid, containing 1,000th of nitric acid. It is coloured in the same way by all the salts that yield oxygen readily, and morphia, brucia, and strychnia are coloured in the same way. When boiled with a concentrated lye of potass, it appears to give rise to the formation of a peculiar acid. It is distinguished from morphia by giving no blue

with permuriate of iron. With hydrochloric acid narcotina forms a salt, which crystallises from its alcoholic solution. When this is boiled with solution of the bichloride of platinum, it yields a new acid termed the *opianic*, and a new base, cotarnia.

Morphia, $C_{34}H_{19}NO_6$. This is the most abundant base in opium. It may be procured directly from opium, or by decomposing a salt of morphia, as the muriate in solution with excess of ammonia, when the morphia falls and can be taken up by boiling alcohol, and crystallised from the solution. From opium itself it may be obtained by macerating opium cut into pieces in water, and expressing the mass through cloth from time to time, and evaporating the cold watery infusion to the consistence of an extract. This is again digested in cold water, which leaves a brown matter, containing especially narcotine. The same process can be repeated upon the second watery infusion. Into the last watery solution ammonia is added by degrees. The precipitate produced is digested with alcohol, which removes the resinoid matter and leaves the morphia. The residue is then taken up by boiling alcohol, and morphia crystallises on cooling. The alcohol is then driven off in part, and the mother waters furnish a new deposit of morphia. The morphia can be decolorised if necessary by animal charcoal.

Morphia crystallises in rectangular prisms or octahedrons. The crystals lose two eqts. of water on being heated. They decompose by a heat below $572^{\circ}$, but before any gas has been given off the morphia has changed its nature. Cold water only dissolves a fractional part of morphia, boiling water $\frac{1}{500}$th, cold alcohol $\frac{1}{40}$th, and boiling alcohol $\frac{1}{30}$th. It is insoluble in ether. Fats and essential oils dissolve it. Its solutions have an alkaline reaction; solution of potass dissolves it entirely, and furnishes a means of separating it from narcotine. Nitric acid gives it an intense red colour. It decomposes iodic acid, and disengages iodine. It gives a blue colour to a solution of perchloride of iron and chloride of gold. Its salts have the general characters of the base. Good opium may contain 10 per cent. of morphia.

*Muriate of Morphia*, $\overset{+}{M}HCl,6HO$, the salt now generally used in medicine is usually prepared by macerating the opium in water frequently, and so dissolving out the meconate; the infusion is then concentrated, and decomposed by chloride of calcium; double decomposition takes place, meconate of lime is precipitated, and muriate of morphia remains in solution. The impure muriate is obtained by evaporation of the solution and crystallisation. The mass of muriate thus obtained is squeezed in a bag, dissolved in hot water and filtered through animal charcoal, and subjected to repeated crystallisation; so prepared it contains codeia. It is soluble in 18 parts of cold water, and its own weight of boiling water, and in alcohol. The sulphate also crystallises with 6 eqts. of water. Morphia may be separated from codeia by means of ammonia, which throws down morphia from the solution of both muriates, but leaves codeia.

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*Other Alkaloids of Opium.*—Thebaina is coloured immediately red on contact with sulphuric acid, containing nitric acid, while with narcotina the change takes place more gradually; pseudomorphia, like morphia, gives a blue colour with persalts of iron, but it is insoluble in absolute alcohol, and very slightly soluble in dilute acids. Narceia is known by the blue colour which fuming hydrochloric acid diluted with a little water makes it take. Papaverine is rendered blue by sulphuric acid; porphyroxine assumes a red colour when treated with muriatic acid; but to give a full account of these subordinate principles would be beyond the limits of this treatise.

*Codeia*, $C_{36}H_{21}NO_6$, may be obtained from the mixed muriates of morphia and codeia, either by the action of ammonia, which throws down the morphia, as already described, and leaves the codeia to crystallise spontaneously from the mother liquid, or by the action of potass on the mixed muriates, which dissolves the morphia and leaves the codeia. The residual mass must then be purified, first by solution in ether, and then in water. Codeia crystallises from its solutions in anhydrous colourless octahedrons. It is soluble in 80 parts of cold, and 17 of boiling water; its solutions are strongly alkaline. Its salts possess none of the reactions of salts of morphia, and are, besides, distinguished from these in being precipitated freely by tannine. The salts have an extreme bitterness, and are supposed to have great activity, and to possess the soothing properties without the narcotic effects of morphia.

STRYCHNIA, $C^{44}H^{46}N_3O_4$, is found in several species of strychnos, accompanied with an acid termed igasuric, supposed to be a modification of the lactic, and with another principle termed brucia. It is prepared by boiling raspings of nux vomica with water acidulated with $\frac{1}{8}$th of sulphuric acid, expressing the liquor and precipitating it with an excess of milk of lime. The precipitate is to be collected, dried, and treated with boiling alcohol. The strychnia is dissolved and crystallises on cooling. It must be again dissolved in boiling alcohol, after being washed with cold alcohol. The mother waters yield more on concentration, and in the end yield brucia.

*Strychnia* crystallises in octahedrons or quadrilateral prisms. It is colourless, inodorous, and excessively bitter. Heat decomposes it without melting it. It is almost insoluble in water, in dilute alcohol, and ether; absolute alcohol dissolves 5 per cent of it. Treated with caustic potass, it yields leucoline. Nitric acid dissolves it without acting upon it, unless very concentrated; it then colours it yellow. Concentrated sulphuric acid colours it deep red, and then violet. It becomes of a violet colour in contact with the binoxide of lead, or bichromate of potass and nitric or sulphuric acid, which colour in a few minutes disappears. Strychnia is very soluble in weak acids. The salts have all the properties of their base, are well-defined, and crystallisable.

*Brucia*, $C_{46}H_{26}N_2O_8$, exists in the mother liquor which has served to prepare strychnia, being much the more soluble of the two. This mother liquor being evaporated to a syrup, is to have sulphuric acid

added to it slightly in excess. After some days, crystals are deposited, which are to be squeezed in a cloth, boiled with animal charcoal, and the filtered liquid precipitated by ammonia. It may also be prepared from the bark of brucia antidyscuterica, by boiling it with water repeatedly, treating the decoctions with oxalic acid, then evaporating to an extract, and digesting the extract with alcohol at 32°. After removing the alcoholic solution, the residual oxalate of brucia is to be decomposed by boiling with magnesia. The brucia is then to be dissolved out, and crystallised by means of alcohol. Brucia crystallises from its alcoholic solutions in rhombic prisms. It is soluble in 850 parts of cold and 500 of boiling water; very soluble in alcohol, and insoluble in ether. Nitric acid communicates to it a blood-red tint, and, at the same time, a volatile product is formed, consisting of nitrous ether. The salts of brucia are soluble and crystalline, and have the same reactions as the base.

A vast number of vegetable alkaloidal principles have been described; of these the more important are caffeine and theobromine.

*Caffeine, Theine, or Guaranine,* $C_{14}H_{10}N_4O_4$, is prepared by making a decoction of coffee or tea; precipitating this by sugar of lead, when a compound of tannine and caffeine falls as a caffeotannate of lead; decomposing this by sulphuretted hydrogen, and concentrating the liquid, when the caffeine crystallises; and may be purified by resolution in and crystallisation from either water or alcohol. Caffeine crystallises in long silky needles, which at 212° lose 2 eqts. of water, melt at 250°, and sublime at 723°. It is, as might be supposed, soluble in water and alcohol, less so in ether. Caustic potass and baryta decompose it, disengaging ammonia. Nitric acid boiled with it, gives at first, a yellow liquid, which acquires a purple colour with ammonia, but which afterwards becomes colourless, is not reddened by ammonia, and deposits white crystals. Caffeine is a very weak base; it is bitter, but the peculiar properties of the substances into whose composition it enters may depend as much on oily and aromatic substances with which it is combined, as on its own properties. It is poisonous to the lower animals.* (It is singular that drinks from plants so very different, produced and used in such diverse parts of the world, and for such similar purposes, as coffee, tea, and the tea of Paraguay, should be found to contain the same principle.)

*Theobromine,* $C_{12}H_8N_4O_4$, is obtained from the cocoa beans by the same process as caffeine. Its formula is that of caffeine minus bicarburetted hydrogen, $C_2H_2$; it is a crystalline powder, which, kept for some time in the mouth, tastes bitter, does not alter in the air, is volatilised at 482°, leaving a residuum of carbon. It is scarcely soluble in boiling water, still less so in alcohol and ether. Barytic water dissolves it without disengaging ammonia.

* Unpublished experiments.

To this list might very properly be added Aconitina and Atropia, besides others of less importance.

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### SECT. III.—ALKALIES OF ANIMAL ORIGIN.

These principles have urea for a type; their formula is very simple, and chemical equivalents low.

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| Urea | $C_2H_4N_2O_2$ |
| Sugar of gelatine | $C_4H_5NO_4$ |
| Guanine | $C_{10}H_5N_5O_2$ |
| Xanthine | $C_{10}H_2N_2O$   (Urinary Calculi) |
| Creatinine | $C_8H_7N_3O_2$ |
| Creatine | $C_8H_9N_3O_4$ |
| Sarcosine | $C_6H_7NO_4$ |
| Cystine | $C_6H_8NO_4S_2$   (Urinary Calculi) |

Sugar of gelatine, *glycocoll*, $C_5H_4NO_3,HO$, is prepared most readily by boiling one part of pure hippuric acid with four times its weight of concentrated hydrochloric acid, heating until the hippuric acid is completely dissolved, adding water after half an hour has elapsed since solution, and then allowing the solution to cool. Benzoic acid solidifies into a crystalline mass, and the whole is thrown upon a filter and washed, until the washings cease to have an acid taste. The liquor is then evaporated in the water bath, and the residue redissolved in water and evaporated afresh; in this way the hydrochlorate of glycocoll is obtained quite pure. Ammonia is then added, until an alkaline reaction is obtained; then, by pouring in absolute alcohol, a white precipitate of small crystals of glycocoll is obtained. Sal-ammoniac remains dissolved in the alcohol. The liquid should be left to itself for some time after the addition of the alcohol; then the precipitate washed on a filter with absolute alcohol. Glycocoll is formed by the action of sulphuric acid on gelatine, and then saturating with lime; also by the action of alkalies on gelatine. Glycocoll has a sweet taste, is inodorous, neutral in its reactions, soluble in rather more than four parts of cold water, nearly insoluble in alcohol and ether. A very small quantity of glycocoll added to solution of sulphate of copper, prevents caustic potass precipitating the copper, and gives a fine blue colour to the liquid. Glycocoll is not fermentable.

*Guanine*, $C_{10}H_5N_5O_2$, is obtained by treating guano by a diluted milk of lime, until the liquid is coloured slightly green by boiling, filtering, and neutralising by hydrochloric acid. After some hours the guanine, mixed with sulphuric acid, is deposited of a flesh colour. The precipitate is treated with boiling hydrochloric acid, when guanine alone dissolves. The cooling of the acid liquor gives the hydrochlorate of guanine. On decomposing this salt by ammonia, pure

guanine is obtained. Guano yields one per cent. of it. It is a clear yellow crystalline substance, which can be heated to 448° without losing weight. Heated with chlorate of potass and hydrochloric acid, it forms *guanic acid*.

*Creatinine*, $C_3H_7N_3O_2$. *Creatine*, $C_3H_9N_3O_4,2HO$. These principles are both very important in the animal economy, being very extensively diffused. The latter is altogether neutral. Creatine is obtained either from the flesh of animals, or the fresh urine of man. The flesh of the ox may be cut into pieces, and a watery extract formed by the help of expression. The liquid is then heated in the water bath until separation of the albumen by coagulation. The liquid is separated from the albumen by filtration, and is obtained colourless, and with an acid reaction. It is neutralised by baryta, and evaporated in the water bath. The film which forms on the surface is removed, and when the liquid has acquired the consistence of a syrup, it is left to itself in a warm place. Brilliant short acicular crystals form. These crystals are generally right rectangular or rhomboidal prisms. (See fig. 50.) The crystals contain 2 eqts. of water, which they lose at 212°, and are decomposed at a more elevated temperature; they have a rough taste. They are inodorous, and do not alter in the air. Creatine is soluble in 74·4 parts of cold water, very soluble in boiling water, very insoluble in alcohol, and quite so in ether.

If a solution of creatine is boiled in barytic water, the creatine will be resolved into ammonia and carbonic acid, or into urea and sarcosine. In strong acids, and under their influence, it is transformed, losing water, into creatinine. Creatine contains the elements of glycocoll and ammonia. Creatine is an excrementitial principle, like urea. Creatinine exists in the muscles, as well as creatine; it also exists in the urine; like creatine, it exists in the fluid form. It differs from creatine in having a distinct alkaline reaction, and forming crystallisable salts with acids. Creatinine can be prepared from the urine putrefied, by boiling this with milk of lime, as long as ammonia is developed, then filtering, evaporating, and mixing the syrupy residue with chloride of zinc, in the proportion of one part of this to 32 of the residue; after some days a double salt of chloride of zinc and creatinine crystallises in yellow mammillated crystals. This is well washed with water, dissolved in boiling water, and precipitated with hydrate of oxide of lead until the solution becomes very alkaline. The creatinine then remains in solution. Some traces of lead and colouring matter are removed by animal charcoal. Or it is only necessary to treat creatine with concentrated hydrochloric acid, evaporating until the excess of muriatic acid is dissipated, and decomposing the muriate of creatinine by means of hydrated oxide of lead. Creatinine crystallises in brilliant colourless crystals, which contain no water of crystallisation. It has a caustic taste, is inodorous, soluble in 11·5 parts of water at the ordinary temperature, more easily in hot water, in 100 parts of cold alcohol, and is very soluble in boiling alcohol, slightly soluble in ether. It has active alkaline and basic properties. When urine is exposed to the air for some weeks, much creatinine but no

creatine is found in it. Creatinine crystallises generally in right rhombic prisms or square plates (see fig. 5).

*Sarcosine*, $C_6H_7NO_4$, is obtained by adding to a boiling and saturated solution of creatine ten times its weight of crystallised hydrate of baryta; the liquid becomes troubled by long-continued boiling, ammonia is given off, and carbonate of baryta thrown down. The excess of baryta is got rid of by a current of carbonic acid gas; and the liquid filtered and evaporated, soon becomes a mass of large transparent and inodorous plates. These are crystals of sarcosine, which can be purified by converting them into sulphate, which is to be decomposed afresh with carbonate of baryta added to the watery solution. Sarcosine crystallises in right rhombic prisms, which are colourless and transparent, very soluble in water, slightly so in alcohol, and insoluble in ether. They are not altered at 212°, fuse a little above that, and are volatilised without residue by a higher temperature. In forming it, creatine is resolved into sarcosine and urea.

Among animal principles, not yet described, may be mentioned cholesterine, inosite, inosic, and pneumic acids, as of some importance.

*Cholesterine*, $C_{25}H_{22}O$, is found ready formed in the blood, bile, liver, brain, nerves, the crystalline lens of the eye, and in the fæces. It is also found in several abnormal productions. It is easiest obtained from biliary calculi, by dissolving the calculi, first well washed in boiling alcohol, when, on cooling, the cholesterine at once crystallises. It may be obtained by a similar process from inspissated bile, using ether instead of alcohol, and digesting the residue left by the ether with a caustic alkali to remove fats. Cholesterine is a neutral body, white, pearly, and insipid, inodorous, insoluble in water, only slightly so in cold alcohol. It crystallises in thin rectangular or rhomboidal scales. Its sp. gr. is 1·03. It melts at 278°. (See figs. 52, 53.)

*Inosite*, $C_{12}H_{16}O_{16}$, is obtained from the mother waters proceeding from the juice of meat from which the creatine has been obtained, and which have been distilled with sulphuric acid to remove the volatile acids. Oxide of barium is to be added to the liquid, and after the sulphate of baryta has been precipitated, crystals of sulphate of potass form, which are to be separated; then alcohol is added to the liquid until it begins to be troubled, crystals of sulphate of soda form, and others like sulphate of lime; those last are inosite, which are to be separated partly mechanically and partly by boiling alcohol diluted and acidulated with sulphuric acid. It crystallises in rectangular prisms, which are very soluble in water, difficultly so in pure alcohol, and are not changed by boiling in dilute acids.

*Inosic acid* exists in the flesh in the form of inosate of potass. The inosic acid is best extracted from the flesh of the fowl, by cutting it to pieces, macerating it, and kneading it with water, and, finally, expressing it through a bag. The fluid is then boiled, which separates it from albumen, and phosphoric acid is precipitated as phosphate of barytes, the liquor is filtered, and evaporated in a water bath, and creatine crystallises; finally, the fluid is treated with alcohol and inosic acid crystallises. Inosic acid is uncrystallisable; when pure, it

forms a liquid which cannot be dried; it becomes solid and hard when alcohol is added to the liquid acid. When heated to a moderate temperature, it is decomposed, diffusing an odour of roast meat. It is very soluble in water, completely soluble in alcohol, or ether. It reddens litmus, and forms salts with bases. It is obtained by decomposing carefully its salts of inosate of potass, or baryta, by a more powerful acid; the preceding process yields a mixture of inosate of baryta with inosic acid. Its formula is given $C_{10}H_6N_2O_{10},HO$.

*Pneumic Acid* is a principle which exists in the *parenchyma* of the lung, and gives it the power of reddening litmus. It is supposed to be formed by decomposition, and to play an important part there by decomposing carbonates, and giving rise to a portion of the carbonic acid exhaled in respiration. It is obtained from the tissue of the lung by a complicated process. The chief part of this process is to heat the juice extracted from the pulmonary tissue so as to coagulate albumen, neutralise by baryta, precipitate the pneumate of copper by adding sulphate of copper, and decompose the pneumate of copper by sulphuretted hydrogen. Pneumic acid crystallises in various forms.

## CHAPTER 9.

In this division of the work it shall be our object to give a brief but comprehensive summary of what is known of the composition of the principal animal fluids, as milk, blood, bile, urine, the saliva, the gastric and pancreatic juices, of some of the solids, and the theory of food.

### I. MILK.

Milk is of very similar constitution from whatever animal it is derived; examined by the microscope, it is found to be composed of a number of globules floating in a clear fluid. The globules are round, and of different sizes (see fig. 54). These globules consist of fat surrounded with an envelope of albuminous nature. When treated with acetic acid, the envelope is dissolved, and the butter or fat escapes. When milk is churned, this envelope is mechanically broken. When milk is allowed to rest for some time, the globules float to the top and form cream, and the churning of this separates the bulbs from the envelopes, which float in residual water. The fluid mixed with the butter containing caseine in solution, the butter must be washed to free it from residual caseine, which being a fermentative principle readily undergoes putrefaction. It is on this account that salt is also added to preserve butter. The sourness of milk is owing to the conversion of its sugar into lactic acid, which then coagulates the caseine. Thus curds are produced. The same effect is produced by the stomach

of the calf (*rennet*), and then, by a filtration through a sieve, the coagulated caseine remains, and the whey passes through. (See fig. 55.) Milk in the human subject contains about 116 parts of solids, and 884 parts of water. The solids being composed of, according to one analysis, sugar 47, fat 25, caseine 37, and salts 2. But in other analyses somewhat different results have been obtained. The milk of animals is generally richer in solids than that of woman. In the salts those generally found in the animal fluids exist. Perhaps it might be found, if analyses of milk were made more minute, hardly any of those said to exist in the animal fluids might not be detected. Milk in disease may be found mixed with blood or pus, recognisable by means of the microscope. After pregnancy the escape of some of the fat from the envelopes of the globules produces the appearance of the colostrum. Milk has a sp. gr. of about 1030.

## II. BLOOD.

Blood, examined by the microscope, is found to be composed of a colourless liquid, holding in solution globules either white or coloured. The red and white globules of human blood are represented in fig. 56. The latter are round, granular, and normally in small proportion, somewhat larger than the red globules, which latter present a nucleus and a surrounding rim, or envelope. The former are not so susceptible to the action of acetic acid as the latter, which are disaggregated and soon dissolved by it, while the former are rendered smooth and transparent. According to one ultimate analysis, the composition of the globules of human blood would be, apart from the ash, C, 55·1; H, 7·1; N, 17·2; O, 20·6. The mineral constituents of the blood-globules are very numerous—salts of potass, lime, and magnesia exist there, chlorine, fluorine, sulphur, iron, manganese, copper, lead, and silica. The presence of these metallic substances may be easily detected by collecting the blood, diluted with two or three times its bulk of water, in a flask of gaseous chlorine, agitating it well, then passing it through linen, drying and calcining the liquid. The saline residue is to be dissolved in muriatic acid, and the solution gently evaporated to dryness. The residue is to be redissolved in water, which leaves the silica. The metals are found in the solution. Many theories have been formed with regard to the nature of the colouring matter of the blood.

It is now agreed that the colour of the blood is due to a principle termed hematine or hematosine.

*Hematine* is a principle essentially characterised by its red colour, which, in the normal state, exists only in the blood globules. It must not be confounded with the *globuline*, which constitutes the mass of the blood corpuscles. Its proportion in the whole blood has been given at from 2 to 10 per cent., and in the globules themselves at about 12 per cent. ordinarily. Hematine exists in the blood in a semisolid state, which readily passes into a more solid or fluid state under slight influences. Hematine, viewed by a transparent light, is of a yellowish-red colour; by a reflected light its colour is that of the

blood. It easily alters its colour under slight influences, and under some of these, different names have been given to it. When obtained it is an amorphous, brownish, pulverulent mass, insoluble in water, soluble in boiling alcohol and ether, and colouring its solutions red. It is insoluble in water and acids, slightly soluble in potass. It contains 7 per cent. of its weight of iron, which seems to exist there in an elementary form. Its composition in the ox has been given—C, 65·34; H, 5·44; N, 10·39; O, 11·88; Fe, 6·93.

Along with globuline, salts, and fats, it forms the blood globules. It is supposed in some unknown way to contribute, or to form by its modifications, the colouring matters of the bile, the urine, &c. It is obtained from the blood by a complicated process.

*Globuline,* which may be described as an albuminous principle, forming the mass of the blood globules, exists in the blood in a proportion varying of course with that of the blood globules, of which it forms the greater part, that of the fat being inconsiderable. Its proportion has been calculated at 87·5 per cent. of the globules. It exists in the semi-solid state in the blood, and floats insoluble in the serum. It is soluble, however, in water, and then resembles albumen, differing from the latter chiefly in the higher temperature required to coagulate it, requiring a temperature of 180°, or even upwards. It is also soluble to some extent in boiling water. It is also less soluble in acetic acid. It is obtained by dissolving the blood globules in boiling alcohol, containing a little carbonate of soda. When ether is added to the liquor, the globuline is precipitated as a white mass, and the colouring matter and fats remain in solution.

It is well known that when the blood coagulates, it separates into two parts, the serum, and crassamentum, or clot. The latter contains the globules, with fibrine, some fats, &c.; the former is chiefly composed of a solution of albumen and salts. Both these contain extractive matters.[*] Perhaps the following analyses are calculated to give as good an idea as any others of the composition of blood.

|  | Male. | Female. |
| --- | --- | --- |
| Water . . . . . . . . . . | 779·000 | 791·100 |
| Globules . . . . . . . . . | 141·100 | 127·200 |
| Albumen . . . . . . . . | 69 400 | 70 500 |
| Fibrine . . . . . . . . . | 2·200 | 2·200 |
| Extractive matters, free salts . . . | 6·800 | 7·400 |
| Fatty matters . . . . . . . . | 1·600 | 1·620 |
| †Seroline (peculiar fatty matter) . | 0·020 | 0·020 |
| Phosphuretted fatty matter . . . | 0·488 | 0·464 |
| Cholesterine . . . . . . . . | 0·088 | 0·090 |
| Saponified fats . . . . . . . | 1·004 | 1·046 |
| Chloride of sodium . . . . . . | 3·100 | 3·900 |
| Soluble salts . . . . . . . . | 2·500 | 2·900 |
| Insoluble phosphates . . . . . | 0·334 | 0·354 |
| Iron . . . . . . . . . . | 0·566 | 0·541 |

* The specific gravity of blood is about 1056.
† A mixture, in all probability, of other substances.

Many more minute analyses have been published, but this is, on the whole, as probable a view of the general constitution of the blood as has yet been given. Minute analyses of the blood might be pushed to a great extent, since the variety of compounds, principles, and substances it contains, is probably much greater than is supposed. For practical purposes, in most diseases, it may be generally deemed sufficient to determine the amount of the principal elements according to the following formula :—

> Water.
> Solids.
> Globules.
> Fibrine.
> Solids of serum.
> Salts.
> Fatty matters.

In particular diseases, as diabetes, in the analysis of poisons, &c. it is, of course, necessary to carry out the modes of analysis requisite to detect the particular substances supposed to exist, and sometimes to determine their amount; and perhaps it would be well if we had tables of the constitution of blood disease, in which the analyses, by the *same method*, had not been carried further than the principal elements. Objections may be made to almost every method of analysis of blood; but few could be made to its comparative results. Two methods may be described: 1st, the method by which the blood is received into a single vessel, and allowed to coagulate; and 2nd, that by which it is obtained in two separate proportions, which are to be treated separately. Both these methods are only applicable to rather considerable quantities of blood, as from not less than 4 to 10 ounces.

By the first method the blood is to be received into a counter-poised glass vessel, or other vessel whose weight is known. The vessel should then be covered with a glass plate and set aside for about twenty-four hours. When coagulation is completed a few ounces of the serum are to be removed, weighed in a vessel of known weight, and evaporated to dryness, and the vessel again weighed. The serum is then to be poured off from the clot as carefully as possible, so as to remove none of the colouring matter, and the clot is to be dried by filtering paper. The clot is then to be cut in halves by a sharp knife, and these halves weighed, and made equal by addition or subtraction. One half is to be placed on a filter of fine cloth, and washed until at last the fibrine is left white. This is to be pressed, dried in a salt-water bath, and weighed. This, of course, represents half the fibrine in the whole blood; but as it is more easy to talk of this division of the clot than always to make it, whatever proportion the portion treated for fibrine of clot bears to the whole clot, such will be the proportion of the fibrine obtained to the whole fibrine of the clot. The other portion of the clot is to be evaporated to dryness as the serum was; and taking into consideration the pro-

portion it bore to the whole clot, the result of the evaporation will enable us to get the amount of solids in the clot. We thus get the amount of water and solids in the whole blood by adding the results derived from the serum and the clot; or we have obtained—

Solids of scrum—and Fibrine.
Water.

It must next be considered that the water in the clot must have been water corresponding to a certain amount of serum, and the result of the drying of the serum will tell, as by a rule of three comparison, how much solid this must have been. This amount of solid, added to the amount of fibrine subtracted from the weight of the dried clot, will give the amount of globules.

The formula will now give:—

Water.
Solids.
Globules.
Solids of serum.
Fibrine.

The salts of iron may be determined by incinerating a certain portion of the dried clot and dried serum in the proportion in which they exist in the blood in a platinum crucible; and the fats somewhat coarsely, by digesting the residual dried clot with cold and hot alcohol and ether.

The second method operates in a different way; the blood is collected in three separate portions. Suppose the quantity to be drawn be 6 ounces. First, $1\frac{1}{2}$ ounce is drawn and set aside; then 3 ounces are drawn into another vessel; and, lastly, $1\frac{1}{2}$ ounce is drawn and added to the first $1\frac{1}{2}$ ounce. The object of this is to have the two portions now thus obtained of the same composition, as it is asserted that the blood first drawn differs in constitution from that drawn last. One of the portions is then stirred or whipped with a stick (the end of a pen answers well), until the fibrine coagulates around it. This washed and dried gives at once the amount of fibrine. The other portion is allowed to coagulate, and the whole clot dried and weighed as before. The process, save the necessity for washing a portion of the clot for fibrine, is now the same as in the former method.

### III. BILE.

Bile is a green fluid of different hues, of a bitter taste, and sickly smell. It is slightly alkaline, of a thick consistence. In mammiferous animals, it consists of from 8 to 10 per cent. of solids; more dilute in birds, and more concentrated in fishes. Ox bile has a sp. gr. of 1·026. It may be mixed with water in all directions, and forms a kind of soapy solution. It is not coagulated by boiling, and evaporated to dryness it gives a green resinoid mass, which can be almost entirely re-dissolved in water; dried bile is almost entirely soluble in

aleohol, with the exeeption of some mucus and eoagulated albumen. The colouring matter of the bile is removed when its aleoholie solution is boiled with animal eharcoal. When a eolourless and coneentrated alcoholic solution of bile is agitated with twice its volume of ether, the resinoid part separates as a thick syrup, while the cholesterine and fatty matters remain dissolved in the ether. When the ether is evaporated, the cholesterine crystallises. The insoluble resinoid portion carries with it the soda, muriates, and alkaline, and earthy phosphates. These salts, which are obtained by incineration, amount to 16·5 per cent. of the dried bile. When the residnal alcoholic solution is evaporated to dryness, the result is a solid friable mass, solnble in water and alcohol. Solution of potass acts upon the aqueous solntion as on a solntion of soap, separating the bile as a thick and consistent syrup. Acetic and oxalic acids do not affect the watcry solution. The mineral acids produce a slight preeipitate. The nentral acetate of lead produces a preeipitatc, but the liqnid then becomes acid, and the acetate of lead has no further effect until it is rendered neutral. Nitrate of silver gives a white prccipitate which soon becomes brown. There are several tests for bile. In the nrine its presence may gencrally be detected by pouring a few drops of nitric acid into the urine, in a thin layer at the bottom of a porcelain dish, when several iridescent opaline colours appear; but the best test is to treat the liquid supposcd to contain it with two-thirds of concentrated sulphmric acid, added drop by drop, slowly, so that the temperatnre may not rise above 120°, and then adding from 2 to 5 drops of a solntion of raw sugar, of 1 of sngar, and 4 or 5 of water, when a fine red colonr is prodnced.

    Thc idea now generally entertained of the eomposition of bile is that it is essentially a compound of soda salts formed by two acids, the cholic and choleic, which are capable of being themselves resolved into other principles. This idea is thus derived:—When bile is evaporated by the water bath, then dried *in vacuo*, and an extract formed in absolute alcohol, and the filtered solntion mixed with ether gradually added, thc liquid assumes a milky aspect, and, at the end of a few days, a erystalline mass is formed. These crystals are not pnre, for, at the same time, another principle of the bile is deposited in resinous drops. The erystals are separated from the liquor, and washed with a mixtnre of alcohol and ether. The mass thus washed is re-dissolved in water, and a solntion of acetate of lead added, which precipitates the cholate of lead. This preeipitatc is decomposed by carbonate of soda. The solution formed is evaporated, and the residue dissolved in absolute alcohol, from which solntion the addition of alcohol ag:ain makes it crystallise. Thc erystals are the cholate of soda. They are to be washcd with aleohol and ether, and dried *in vacuo*. (See fig. 56.) The resinoid drops which are precipitated at the same time with the erystals of cholate of soda, are the other salt of soda, the choleate of soda. Thùs the bile is snpposed to be essentially composed of two salts,—the cholate of soda, which crystallises, and the choleate of soda, which is uncrystallisable. The acid of the first of these salts contains nitrogen, but no sulphur, while the eholcic acid is azotised,

but contains sulphur. It is supposed that these two salts constitute almost the whole bile, with small quantities of cholesterine, fat acids, salts of potass, ammonia, and magnesia. These two acids are transformed by the action of alkalies and mineral acids, the cholic into cholalic acid and glycocoll; the choleic into cholalic acid and taurine, as is shown in the following formulas :—

· Cholic acid, $C_{52}H_{43}O_{12}N$ = cholalic acid, $C_{48}H_{39}O_9$ + glycocoll— $HO = C_4H_4O_3N$.*

Choleic acid, $C_{52}H_{45}O_{14}NS_2$ = cholalic acid, $C_{48}H_{39}O_9$ + taurine— $HO = C_4H_6O_5NS_2$.
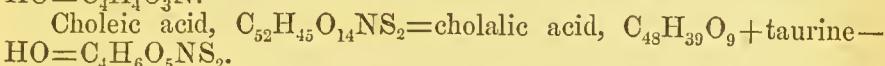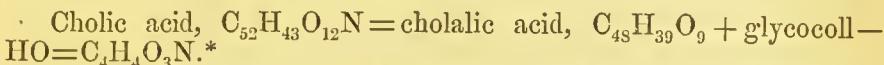
*Cholic Acid* is prepared by dissolving the crystals already spoken of while moist in water, and treating the solution with sulphuric acid. In a few hours crystals form, and some oily drops appear. They are to be washed with water; they are soluble in about 330 parts of cold water and about 120 parts of boiling, and very soluble in alcohol. By treating cholic acid with barytes, the cholalic acid is formed in combination with barytes. On removing the choleate of barytes, glycocoll may be obtained in crystals. Choleic acid is obtained by decomposing the choleate of barytes by muriatic acid.

When solution of neutral acetate of lead is added to bile, cholic acid is precipitated as cholate of lead; when the diacetate is so added, a mixture of cholic and choleic acids falls, along with oxide of lead; when this is decomposed by solution of barytes, a solution of the cholate and choleate of barytes is formed; and when this is boiled with excess of barytes, cholalic acid, glycocoll, and taurine are formed,—and that this last is due to the presence of choleic acid is inferred from its absence when simple cholic acid was treated with barytes.

*Taurine*, $C_4NS_2H_7O_6$. This substance may be obtained directly from bile, by boiling it with muriatic acid, then concentrating and allowing muriate of soda to separate, filtering, and adding to the substance that passes through five times its weight of boiling alcohol, when, after some time, the taurine crystallises.

Biliverdine, the colouring matter of bile, has a certain amount of analogy with the colouring matter of plants. It is essentially characterised by its green colour, passing sometimes to a yellow or brownish green. It is found not only in bile, but it appears in other circumstances,—as, for example, in the placenta of bitches during the last periods of pregnancy. Many of the cases in which it is found in the human subject are well known. Biliverdine is precipitated by sulphate of lime in powder, and by animal charcoal, which, when the bile is filtered through it, allows the colourless bile to pass. Solid biliverdine is a dark green powder, insoluble in water, soluble in alcohol and ether. Its solution is green by reflected light, and of a deep red by transmitted light. Biliverdine contains carbon, oxygen, hydrogen, azote, and iron, in proportions very similar to those of hematine. Biliverdine may be supposed to be formed from hematine by an isomeric catalysis. In order to isolate the colouring matter of the bile, a solu-

* See p. 276.

tion of bile is to be boiled in its volume of water, mixed with a little milk of lime; the solution becomes colourless, and a yellow precipitate is formed. This is to be collected on a filter and dried, and then decomposed by muriatic acid, which unites with the lime, while there is formed a fatty matter of an intense green colour. This green precipitate is agitated with ether in a matrass. The ether dissolves oleic and margaric acids, and acquires a slight green colour. The fat is removed by the ether as completely as possible, and the precipitate is dissolved in alcohol; and on the addition of ether, a strongly coloured matter is deposited, but the ether acquires a bluish green hue. On evaporation, a dark green powder is obtained; very soluble in alcohol and ether, and which, on incineration, yields oxide of iron.

The minute analysis of bile, in the present state of our knowledge of this fluid, would be a matter of great difficulty. But it may be analysed according to a formula, which, if extended in the study of disease, would very likely lead to as important results as those which have already been obtained by such simple formulas in the analysis of diseased blood.

That is to say, we may determine,—

> The water.
> The solids.
> The fats.
> The biliary mucus.
> The cholate and choleate of soda.
> The salts.

A certain quantity of bile, evaporated to dryness in a porcelain dish in a salt-water bath, gives the loss, the water. A certain quantity of the dry residue treated with boiling ether, as long as the ether dissolves anything, and the ether then evaporated, shows by what is obtained from the ether the amount of cholesterine and fats. After the removal of the fatty substances, the residue is to be boiled in alcohol. The alcohol extracts the cholate and choleate of soda, which can be obtained on evaporation in a water bath, mixed with colouring matter. Finally, the salts can be obtained by incinerating a certain quantity of dried bile.

### IV. URINE.

This fluid must be extremely complicated, and probably the limits to its number of contents are only determined by the extent to which the analyses of it are pushed. As almost every element that forms part of the constitution of the globe must be taken into the human system in particular, and as in the process of the destructive digestion of the tissues, whereby those parts of the frame which have become unfit for the performance of the vital functions are removed, these worn out tissues are eliminated almost entirely by the kidneys, it follows that the urine, most probably, contains a great number of ingredients not yet registered in our analyses. It is through the urine, too, chiefly, that poisonous substances are removed from the system. And

as such bodies as copper and lead exist normally in the human body, there is every probability that they exist in the urine. It is as the chief excretion that the urine is especially important to the physician, as the varieties in its component parts give, in many cases, the most precise indications that can be derived of what is going on in the interior of the body.

Urine varies much in specific gravity, according to the time at which it has been emitted, and the attendant circumstances. Urine passed after much drink, especially after diuretic alcoholic drinks, is usually of a pale colour, containing very little solid matter, and therefore of a low specific gravity; that passed just after a full meal has usually the highest specific gravity; and that after sleep the mean density. These are called respectively urina potus, urina chyli, and urina sanguinis, and may vary in a healthy man in specific gravity, from 1007 to 1030.* When first passed, it is generally, though not always, acid; but it soon begins to putrefy with formation of ammonia, and then becomes alkaline.

As the constituents of urine are so various, there is no fixed relation between its specific gravity and the quantity of solids which it may contain.

The quantity of urine in a healthy man passed daily varies greatly, and may vary from 30 to 70 fluid ounces. Very different statements have been given of the composition of normal urine by different observers, although not more so than perhaps what might have been expected from the actual or very probable variations of this fluid; and they agree in a general manner as to the nature of the constituents. The first recorded analysis of any importance by Berzelius gave the following results :—

| | |
|---|---|
| Water | 933·00 |
| Solids | 67·00 |
| | 100·000 |
| Urea | 30·10 |
| Uric acid | 1·00 |
| Lactic acid, lactate of ammonia, and extractive matters | 17·14 |
| Mucus | 0·32 |
| Sulphate of potash | 3·71 |
| Sulphate of soda | 3·16 |
| Phosphate of soda | 2·94 |
| Biphosphate of ammonia | 1·65 |
| Chloride of sodium | 4·45 |
| Muriate of ammonia | 1·50 |
| Phosphate of lime and magnesia | 1·00 |
| Silica | 0·03 |
| | 67·00 |

* In disease, very great variations in the specific gravity are found, especially in Bright's disease of the kidneys, where it is very low, and diabetes, where it is high.

Most of the analyses made since the one just quoted give only about half the quantities of urea and urie acid given in this analysis, but there are not wanting some which appear to confirm its results. The results above given may, on the whole, be regarded as very near the composition of strong healthy urine, but with excess of urea and uric acid, and some excess of extractive matter, lactic acid, and lactates.

When the urine is dried it shows crystals under the microscope like those in fig. 57.

The analysis of the urine may be directed either to the determination of its normal constituents and their respective proportions, or to some principles (in quality or quantity) likewise introduced in disease.

A very simple analysis, but a very useful one, consists in fulfilling the following formula, noting, first, the sp. gr. of the fluid, its acidity or alkalinity, its freedom from deposits 'or the reverse, the quantity passed in the twenty-four hours, of which an average specimen may be taken for analysis by collecting the whole urine of twenty-four hours.

> The water.
> The solids.
> The solids destructible by heat.
> The residual salts.
> The urea.
> The urie acid.

For this purpose it is only necessary to weigh a certain quantity (say 1000 grs.) of the urine in a weighed or counterpoised evaporating basin ; evaporate to dryness in a water bath until the urine ceases to lose weight, and ascertain the loss, which is water. The residuum carefully burnt in a large platinum crucible previously weighed, and then burnt to whiteness, will give the amount of destructible organic matter, and the amount of residual ash or fixed salts, which can be tested as if they had been derived from a mineral water. The urie acid can easily be ascertained by taking 1000 grains and adding a few drops of nitric acid, and allowing the urine to stand for twenty-four hours, at the end of which a sediment of urie acid will be found ; and on decanting the greater part of the urine, and washing the remaining portion well with the sediment washed out on a weighed filter, the amount of urie acid can be weighed.

Urea is usually quantitatively ascertained in the mode described for procuring it at page 222, but it may be estimated in a more direct manner by the reaction of nitrate of mercury on urine itself.*

With regard to urine in disease, its numerous modifications require the conjoined aid of chemistry and the microscope.

The chief substances in excess in the urine, besides the occasional presence of mucus, chyle, and blood, are crystals and deposits of the ammoniaco-magnesian phosphate, the urates, and oxalates, representations of which will be found at the end of this work.

## Urinary Calculi.

Calculi vary greatly in size, but are formed on the same principle from the gradual agglomeration of deposits. They are conveniently divided into two classes:—I. Those soluble in solutions of caustic soda or potass; and II. Those which are insoluble in these solutions. The former class includes—1. Uric or lithic acid; 2. Urate of ammonia and urates; 3. Xanthic oxide, or xanthine; and 4. Cystic oxide, or cystine. The calculi insoluble in solutions of caustic potass and soda are—1. The phosphate of lime; 2. The ammoniaco-magnesian phosphate; 3. The fusible calculus, a mixture of the ammoniaco-magnesian and phosphate of lime; and 4. The oxalate of ammonia.

---

### I.—Calculi soluble in solutions of potass and soda.

It will be observed that these calculi are all to be regarded as immediate principles, as anatomical elements of the human body.

1. *Uric Acid Calculus.*—It has been said, page 225, that uric acid rarely exists in the urine *normally* in the free state, but it forms most frequently either the nucleus or some part of calculi. When uric acid is found in the urine deposited in the free state, its presence is ascribed to the decomposition of the urate of soda existing normally in the urine by free lactic acid, for if the urine be heated to the temperature of the body, the deposit is not redissolved. When deposited from the urine, it crystallises very regular. The most frequent form of these crystals has been already described. In general, the calculi are yellowish and smooth, sometimes crystalline in appearance. Besides their being soluble in soda, they are detected by their reaction with nitric acid when heated, and ammonia is added, when the purple colour of murexide is produced.

2. *Urate of Ammonia* calculus is distinguished from uric acid by its solution in the caustic alkalies, with evolution of ammonia.

3. *Xanthic Oxide, Xanthine,* $C_5H_2N_2O_2$. This substance very rarely occurs. It is obtained by dissolving the calculus supposed to contain it in potash, then precipitating from the solution by means of carbonic acid. It is found as a yellowish or reddish hard, laminated calculus. It is soluble in soda, and thrown down by acetic acid. It is distinguished from cystine by its insolubility in oxalic and muriatic acids. When heated with nitric acid, of sp. gr. below 1·350, it leaves a yellowish substance, deliquescent; but fuming nitric acid, of sp. gr. approaching 1·50, dissolves it rapidly, and forms a reddish liquid, which, thrown into water, gives the purple hue of murexide. A substance presenting many analogies to xanthine, and called on that account *hypoxanthine,* has been obtained from the spleen.

4. *Cystine, Cystic Oxide,* $C_6H_8NO_4S_2$, exists not frequently in gravel and in calculi. It is, however, more common than the xanthic oxide. The calculi formed by it are generally confusedly crystalline

T

and brittle. It is obtained from the calculus by dissolving it in caustic potass, and treating the filtered solution with acetic acid. Its masses are formed of an agglomeration of fine hexagonal lamella, which can be detected by the microscope (see fig. 59). By this, and its property of yielding a peculiar garlicky smell when heated before the blow-pipe, it can be recognised. It is insoluble in water and alcohol, soluble in alkalies, and in the mineral acids. When heated, it yields ammoniacal products, and leaves a spongy oval mass. It also affords a gas spontaneously inflammable, like phosphuretted hydrogen.

## II.—*Calculi insoluble in caustic potass or soda.*

1. *Phosphate of Lime* or *Bone Earth.* The phosphate of lime is found so extensively in the solids and fluids of the animal body, that it is not surprising it should be found in excess in the urine. The calculi occur in many parts of the body as well as in the bladder. It is recognised by its smoothness, by its solubility in nitric and muriatic acids, and its precipitation by ammonia from the ammoniaco-magnesian phosphate, by its *insolubility* in acetic acid. It is precipitated from the urine whenever this fluid becomes alkaline. It is generally found amorphous in the organism, but it has been found in right rectangular prisms.

2. *Ammoniaco-Magnesian Phosphate*, Triple Phosphate, $NH_32Mg$ $O,PO_5$, and $10HO$, is very seldom found normal in the animal fluids. It appears to be formed in the process of decomposition in the tissues by the ammonia formed during this decomposition becoming combined with the phosphate of magnesia, which salt is found most extensively in the tissues, sometimes in the crystallised form, and has been found as an ingredient in urinary calculi. The bright layer often found on the top of urine which has stood four-and-twenty hours, is formed of crystals of the ammoniaco-magnesian phosphate. In urinary calculi, this salt is generally joined with others. It generally exists solid in the body. The crystals vary in form, but are mostly of a roof-shaped appearance, and are soluble in acetic acid, whence they are thrown down by the addition of ammonia in stellate crystals. The calculi are known by their giving off ammonia before the blow-pipe, and yielding a white residue. When the tissues containing phosphate of magnesia are dissolved in an acid, and ammonia added, the ammoniaco-magnesian phosphate is at once thrown down, generally in star-like dendritic groups (see fig. 60). In the concretions where it exists, it is readily detected by their solution in acetic acid, and precipitation by ammonia.

3. *Fusible Calculus.* It will readily be understood how this calculus can be formed by the junction of the two preceding ones. It may be distinguished by its great friability, even soiling the fingers, by its fusing into a glass before the blow-pipe, and finally, treated with acetic acid the phosphate of lime is left behind, and the triple phosphate is dissolved, when both can be recognised by tests.

4. *Oxalate of Lime* exists often in excess in the urine, where it forms octahedrous or dumb bell crystals. Its characters may often, or generally, be recognised in concretions by their irregular form, brown colour, and hardness. Heated before the blowpipe it is reduced to carbonate of lime, which can be recognised by its well-known properties, effervescing with an acid and becoming alkaline when heated. It is readily soluble in muriatic and nitric acids, from which solution of potass throws down oxalate of lime. It often exists in healthy urine (see fig. 61), and appears to be formed under very variable conditions.

## V. SALIVA, GASTRIC JUICE, ETC.

The saliva is a clear, slightly viscid fluid, secreted from the parotid, sublingual, and submaxillary glands. Its sp. gr. varies from 1·003 to 1·008. It contains from 6 or 7 to 12 parts of solids in the 1·000. Analyses vary with regard to the precise nature of the constituents; but they agree generally in recognising as the principal ingredient a substance called *ptyaline*, which sometimes constitutes a full third of the solids. This is a kind of albumen, precipitated from the saliva by alcohol, but to which fermentative properties are assigned as to diastase. In short, it is supposed to act as a catalytic agent in the animalisation and assimilation of the food. Besides ptyaline, the saliva contains also mucus, chlorides, lactates, and a little free soda, to which it owes its generally alkaline character. During meals, however, it is said not to be alkaline, but acid, as if at this period an acid secretion took place from the salivary organs as from the stomach. Its alkaline sulphocyanide has also been detected by many observers in the saliva, which causes this fluid, when greatly concentrated, to strike a red colour with permuriate of iron.

The gastric juice has been examined chiefly in animals. In the dog it has been found to contain 26 parts in the 1000 of solid matters, composed in great part of an albuminous principle, similar to ptyaline, and to which the name of *pepsine* has been given, of salts chiefly chlorides and phosphates, and of 3 in the 1000 of free muriatic acid. To this principle pepsine an important part in the digestive process has been ascribed. It is obtained by washing the stomach of a pig cut into pieces until putrefaction has commenced. The washings are to be filtered, and precipitated by sugar of lead, and the precipitate washed, and decomposed in suspension in water with sulphuretted hydrogen. The precipitate includes a combination of oxide of lead and pepsine, and albumen and oxide of lead: the latter is precipitated by the SH, the other remains in solution. The solution retains some acetic acid. It is evaporated to the consistence of a syrup, and anhydrous alcohol separates the pepsine in voluminous white flocculi, which are to be washed with alcohol; the free acid requires several new solutions and precipitations with alcohol. It is then dried by the water bath, and there remains a neutral powder, soluble in water, and which, when mixed with muriatic acid, dissolves alimentary substances.

### VI.—SKIN, MUSCLE, BONE, BRAIN, ETC.

The *skin* consists of an outward covering, the cuticle or epidermis, of the true skin or corium, and of a vascular network on the corium, which has been called rete mucosum. The epidermis is little subject to decomposition, and is insoluble in water, alcohol, and dilute acids. Concentrated nitric and sulphuric acids soften and dissolve it. The caustic alkalies also dissolve it, but not their carbonates. It does not combine with tannine. Corns, horns, hoofs, hair, &c., may be regarded as modifications of it. Their substance may be regarded as a kind of dry albumen. The cutis or true skin is, for the most part, soluble in water; and the solution, when evaporated, leaves gelatine, its chief constituent. Leather is formed chiefly by the compounds of gelatine and astringent matters, which are formed by the extraction of the astringent matters in solutions in which the skin is steeped.

In making common leather, the skins are previously soaked in lime water, which enables the skin and hairs to be separated. They are afterwards softened by a putrefaction carried to a certain extent. They are then put into the tan pits, and there exposed to the influence of solutions of tannine and other astringent compounds. The durability of the leather appears to depend, in great part, on the amount of the astringent principle, and especially the tannine absorbed. This amounts in some cases to upwards of one half of the skin.

*Muscle* is composed of water, to the extent of about 75 per cent., in men and the higher animals about 15 of the 25 of solids being fibrine, and the rest composed of matters extractive by alcohol and water, and of salts. The composition of dried flesh is about C, 51·893; H, 7·590; O, 19·127; N, 17·10 and 4·230 of ash, which is nearly that of the blood. Besides albumen, gelatine, and other principles formerly described, there exists in flesh a matter capable of being extracted by water, which is distinguished by its acidity, the other principles being neutral. This is obtained by macerating flesh in cold water and kneading it, then slowly heating to coagulate albumen, when a liquor is obtained which has the smell and taste of meat, but is acid. It contains creatine and creatinine, inosic acid, and several inorganic salts. This watery extract has been called extract of meat. It is supposed to contain nearly all the nutritive properties of the meat whence it is obtained.

*Bones* contain, in the human subject, when dry, in the 100 parts 33·3 of animal matters, 51·04 phosphate of lime, 11·30 carbonate of lime, 2 of fluoride of calcium, 1·16 of other earthy salts, 1·2 of water. When not dried, bones contain 9 or 10 per cent. of water. The bony part of the teeth closely resembles other bones, but the enamel of the teeth contains 84 parts of earthy matter, chiefly phosphate of lime, with carbonate of lime and fluoride of calcium.

*Brain and nervous matter* differ from the other solids, as the flesh, in containing a larger quantity of water, about 80 per cent., more fatty matter, about 5 per cent., about 1½ per cent. of phosphorus, besides

albumen, extractive matters, about 5 per cent. of salts, and those peculiar acids, as the cerebric and oleo-phosphoric acids.

The blood is the type of all the solids and fluids of the body; and the study of it the foundation of all our knowledge on the subject. Already has the application of the present state of our knowledge of its physiological chemistry to disease thrown great light upon the pathology of some diseases; and doubtless, when that knowledge is further advanced, a similar advance in pathological chemistry will take place.

## VII.—FOOD.

It is of course impossible within the limits of this work to give an adequate idea of the subject of animal chemistry. The subjects referred to have been chosen as specimens, and as affording introductions to the student; for the same reason the subject of food forms the material of this chapter, as it is important to show how far wrong even the most eminent men have been led by indulging too much in speculation. The same or similar objections to be made in this part of the subject would be urged with greater force were this work to be extended to many of the chemical theories of respiration which have been propounded, and to their extension to the doctrine of animal heat. As the matter to be now introduced may be considered somewhat controversial, it has been thought expedient to do what has not been done in any other part of the work, viz., to quote authorities. Chemistry, to be truly available in its application to physiology, agriculture, and medicine, must go hand in hand with observation, experiment, and *practice*. Of the mode in which such a union is to be formed, the late Dr. Prout was a memorable example; and although some of his conclusions may have been demurred to, and his observations extended, *none of them was ever refuted*. Up to the present time, he has done more for the advancement of physiology by chemistry than any man of the past or *present* age.

It is now well known that vegetables derive the materials of their nutrition from the air, water, and the inorganic materials of the surface of the globe. From the air they can procure oxygen, azote, and carbon; from water, hydrogen; and these four elements, oxygen, hydrogen, azote, and carbon, along with what they find in the soil, afford everything required for their nutrition. Manures have two objects,—to restore to an exhausted soil the inorganic matters of which it has been deprived by the support of a previous excessive vegetation, and which they cannot dispense with, since they cannot get *them* from the atmosphere; and certain stimulating principles, chiefly nitrogenised and ammoniacal, which, however they may hasten growth, can be dispensed with, since all the organic compounds in plants can, by their wonderful structure, be derived from the atmosphere and the rains of heaven.

An important observation of M. Verdeil, on the mode in which salts insoluble in water enter the tissues of vegetables, may lead to some such explanation of similar facts in the animal kingdom. It appears that in all fertile soils there is a substance, until 1852 unknown, of a very peculiar nature, and soluble in water. This substance is obtained by simply passing distilled water through soil, and evaporating the filtered solution. The extract which remains contains about one half of a principle having some resemblance to sugar, and large quantities of salts and principles insoluble in water, as silica and carbonate of lime, as much as one-third or more of the dried extract being composed of those substances. Other organic matters, as sugar, diastase, &c., have been discovered to have the same effect as this new principle, of combining with mineral or inorganic substances insoluble in water, and rendering them soluble. This observation of M. Verdeil is one of the most striking which have been made of late years.

The mode in which certain infusoria obtain their food is an interesting point. From the almost crystalline forms of many of them, it does not seem improbable that they, like plants, may derive their nourishment from inorganic media; and according to the statement of Spallanzani, that distilled water is as favourable to their development as ordinary water, but that atmospheric air is necessary for this development, and that they are never seen to be produced in infusions boiled in close vessels,* it might seem that this was really the case; if so, we have a provision made for the inhabitants of the water of higher kind, similar to what exists on the surface of the earth, for vegetables derive from the inorganic world all the organic principles requisite to support animal life, and which animals themselves cannot produce, although they can modify them, and give to them *an animalised form*.

The food of animals, at least those of the higher classes, is of three kinds—water, of the necessity of which every one is aware, inorganic substances and salts, and certain organic principles which no animal, as far as it is known, can derive, except from vegetables and other animals.

It could be shown that vegetables cannot exist without these organic compounds so necessary to animals, and all of which can be produced in the former from the combination in various ways of carbon, hydrogen, oxygen, and azote. These organic principles are of two kinds—those which are called azotised, as fibrine, albumen, and caseine, and those which do not contain azote, as starch, sugar, gum, oils, &c. Of late years, the distinction between these two classes has been much insisted on, and it has been maintained, especially by Liebig and his school, perhaps, as we shall see, somewhat too strictly, that the former principles went exclusively to support the essential tissues of the frame, as muscular fibre, and, in short, every tissue whose principal constituent was a nitrogenised substance, while the

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* " Longet sur la Generation," p. 9, " Traité de Physiologie," t. 2. Paris, 1852.

latter were destined to be burnt off in the lungs, and support animal
heat by a pure and simple combustion, analogous to that of the
hydrocarburets in atmospheric air.

This idea of the existence of animal matter ready formed in
plants, and the distinction between these two great classes of food
given by many to Liebig and his school,* is in reality of comparatively
remote origin. Von Bochaute says, "We call that animal matter which
is a substance that nature composes chemically, very manifest in
animals, of which it composes the principal mass, but very obscure in
plants, although it exists there ready formed, and is so essential a
part of them, that it appears to be the base and foundation of their
organisation. Nature composes it in the vegetable economy alone,
whence it passes ready-formed indirectly or directly into animals to
nourish them. It is the principal substance of all the parts of animals,
of the grains or seeds, and of the parenchyma of the roots of plants.
Its analysis gives the same results, whether it is taken from vegetables
or animals." He then gives the analysis according to the coarse
system of the day by destructive distillation. Without quoting
further instances, showing how near towards the close of last century
chemists had approximated to the views deemed more recent, from
the work of MM. Verdeil and Robin, where several are to be found, a
remarkable example may be cited, which is to be found in the
journal entitled "La Médecine eclairée par les Sciences Physiques,"
conducted by Fourcroy, of the date 1791. There is there published
an essay by a M. Hallé, 'on the theory of the animalisation and
assimilation of the aliments.' The following are some of the conclu-
sions of M. Hallé :—

" 1st. We call the change of vegetable into animal substances
animalisation.

" 2nd. By assimilation we mean the passage of alimentary sub-
stances, whether animal or vegetable, into that state which renders
them similar to the parts of which we are composed.

" 3rd. Nutrition supposes animalisation in vegetable aliments, and
assimilation in all alimentary substances.

" 4th. Both of these operations suppose in the alimentary sub-
stances, first, analogies, which render them susceptible of undergoing
these changes, and differences, which render these changes necessary.

    *    *    *    *    *    *

" 6th. We know now that the substances which constitute our
solids, and are transported by our fluids, are all found in our aliments.
The animal aliments contain them ready formed, and the vegetable
contain their analogues.

" 7th. The gelatine or animal jelly has for analogues the vege-
table jellies, whether under the liquid form, as in the juices of a multi-
tude of fruits, or in the dry form, as in the feculas, which contain this
nourishment so diffused in the vegetable kingdom, and which is the
most universal base of the substances which nourish us.

* See Pereira on Diet.

"8th. No one doubts now-a-days that, with some little difference in the proportions, the *vegetable glutinous* matter, so well known in wheat flour, is of absolutely the same nature as the fibrous portion of the blood, and the fibre of our muscles."

It is thus evident that the fundamental doctrines of the formation of the organic immediate principles of the animal frame iu vegetables, have been of very gradual growth. The composition of these vegetable nitrogenised principles is almost identical with the albumen of the blood, $C_{216}N_{27}H_{169}O_{68}S_{2}$, and so with the derivatives. The relation between the fatty elements of the frame, and the starchy and sugary constituents of plants, is readily shown. Thus, it being unnecessary to point out the relationship of starch and sugar, it will only be necessary to give two of the many formulas which may be cited, with the view of showing the facility with which sugar may be turned iuto fat. Thus, 3 eqts. sugar $= C_{36}H_{36}O_{36} - (30,O + 2HO) = 1$ eqt. oleic acid $= C_{36}H_{34}O_{4}$; and 17 eqts. $=$ sugar $17(C_{12}H_{12}O_{12}) - 180$ eqts. of oxygen give 6 eqts. margaric acid $= 6(C_{34}H_{34}O_{4})$; and, in fact, the derivation of most of the fatty principles from starch and sugar is comparatively an easy task, so far as chemical formularising is concerned. Here we see that it only requires a deoxydation to deduce these fatty acids from sugar. And this leads again to call attention to two important parts of the received chemical physiology of the other day, which may now be eousidered greatly shaken, if not overthrown,—the so-called proteine theory, and the doctrine of the almost exclusive use of the starchy and fatty parts of the food, in the support of combustion and animal heat.

Some years ago Mulder concluded from his researches, that all the azotised matters contituting the tissues were formed of a principle to which he gave the name of proteine, with the addition of one or more eqts. of sulphur. Thus, fibriue was 10 of proteine and 1 of sulphur, albumen of the egg the same number of eqts. of proteine with 2 of sulphur, and so forth. From this base, numerous regular compounds were supposed to be formed—regular compounds with acids as with any other base; the fibriue iu the buffy coat was a deutoxide; pyin, the albuminous matter in pus, a teroxide, and so forth. In short, almost all the animal tissues were simply chemical compounds of the same radical. From this theory sprang the system of explaining all the phenomena of the living body by simple chemical formulas, as if such complicated combinations and decompositions admitted of being thus treated, without the aid of the most rigorous and precise observations and experiments. Iu fact, observation and experiment should invariably precede the application of such formulas, which can only be properly applied in explanation of a known fact, not by any means made to serve as a guide to what *must* take place, or to dictate to the observer. However, the many instances in which these formulas ceased to explain the facts which were known to exist, or which came to be observed, and the discovery that the very proteine of Mulder did contain sulphur, overthrew this doctrine.

With regard to the second part of the doctriue, suffice it to remark

here:—first, that the experiments of Bidder and Schmidt prove that in excessive feeding with fat, the animal lost weight from the want of albuminous material; but the quantity of carbonic acid exhaled was diminished. It has been proved that the quantity of fat formed in the tissues of an animal fed with nitrogenised and fatty principles is greater than the quantity of fat consumed can account for.* Fatty principles have been obtained from fibrine. Mr. Gulliver has been able to convert fibrine into a fatty substance;† and lastly, M. Bernard has found that grape sugar conld be detected in large quantity in animals fed exclusively on albuminous food.‡ There can be no question, therefore, that the fatty, starchy, and sugary compounds do not alone support respiration; that pure fat, oil, or sugar cannot produce the albuminous tissues is what might be expected; but it can hardly longer be doubted that albumen itself is capable, to some extent, of forming fats in the tissues and supporting respiration. Now the chief objection made to the derivation of fats from albumen was the difficulty of formularising such a circumstance. However, with a little ingenuity, this might, perhaps, be done; and urea, carbonic acid, water, and a hydrocarburet, *i. e.*, a fatty substance, derived.

However one species of food may temporarily supply the place of another, experience proves that this can only be for a short time.

Magendie found that dogs nourished solely with the fatty, starchy, and sugary class, viz., with sugar, gum, olive oil, and butter, grew lean, became weak, were attacked with ulcerations of the cornea, with abundant secretions from the eyelids, and died in four or five weeks. The application of these facts has been denied by some on the ground of the African caravans being supported in the desert occasionally with gum in crossing the desert, and similar alleged facts, which only prove what must be admitted, viz., that for a time these substances will maintain life: they supply at least one of the elements of nutrition. Numerous experiments and observations prove the incapacity of this class of aliments to support life, so that we may dispense with further references. Nevertheless, it is singular that the one pure kind of food does not support much longer than the other. Thus Tiedmann and Gmelin found a goose, which weighed eight pounds and a half, live forty-four days on boiled rice, which is nearly all of the starchy kind, and weigh five pounds seven ounces; and another goose, which weighed eight pounds and an ounce, lived forty-six days on hard boiled white of egg. At the end of this time it weighed six pounds one ounce and a half.‖ Neither of them was fed on a perfectly pure principle, although the latter was nearly so. In short, it is needless to quote these experiments further. They abundantly prove not only

* "Edinburgh Monthly Medical and Surgical Journal," May, 1853.
† "Medico Chirurgical Transactions,"
‡ "Archives de Médecine," 1848. The admirable researches of M. C. Bernard, are pursued in subsequent numbers of this journal. referred to.

‖ "Recherches Expérimentales," t. 2, p. 231.

that animals will not live upon one or other of the two great divisions of food alone ; but that even the mixed principles of both species pure will not support life : they also prove the importance of the inorganic elements of our food.

It must be remembered, however, in regard to many of these experiments, that the animals subjected to them were not in a normal state—they were necessarily confined. A Hindoo can live long enough on rice, or an Irishman upon potatoes.

Dr. Prout divided aliments into aqueous, saccharine, albuminous, and oleaginous. In the form in which the aliments are used, the inorganic elements of food are taken in along with the organic.

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## CHAP. 10.—INDETERMINATE ORGANIC SUBSTANCES.

THERE are many organic substances whose character it is exceedingly difficult to determine ; sometimes they are ranged as alkaline, sometimes as acid ; and others whose chemical composition is doubtful, or whose isolation from other principles is not certain. Several such have already been noticed, but there are some which especially deserve a notice apart.

*Pectine*, $C_{64}H_{40}O_{56}, 8HO$, exists in the juice of fleshy or pulpy fruits. Its chief remarkable property is that, containing no azote, it has the property of gelatinising in the same way as gelatine itself. It exists in apples, pears, gooseberries, lemons, potatoes, celery, and most other plants, in the stems and leaves. It is accompanied with mucus and with several salts, and has been often confounded with mucus. Pectine exists in two forms—what has been described as a kind of solution, and in what is supposed to be its primitive form, to which the name of *pectose* has been given. In this state it is insoluble in water, alcohol, and ether. Pectose has been supposed to be organised like starch, and to act like a ferment upon pectine, causing it to undergo various changes. On the other hand, pectose is supposed to be converted into pectine by the influence of weak acids, and this is said to account for its presence in ripe fruits. Pectine may be obtained by the addition of alcohol to the juice of fruits, a jelly is then thrown down, of which one portion is insoluble in cold water, while the other, which is the proper pectine, is very soluble. When the tissue of plants is boiled for a long time in dilute acids, and alcohol then added, a gelatinous precipitate is thrown down, which is pectine, and when the same solution takes place with boiling water alone, a similar precipitate is obtained with alcohol. Pectine thus precipitated is

a transparent jelly, which, if dried in thin plates, does not easily dissolve in water, but rather swells, while fresh pectine very readily dissolves. Nitric acid acts upon it as it does on sugar, converting it into mucic and oxalic acids. When pectine is boiled with water it changes into *parapectine* and precipitates neutral acetate of lead, while pectine itself only precipitates the sub-acetate. Long-continued boiling with weak acids changes pectine into *metapectine*, which has weak acid properties and precipitates chloride of barium, while *very long-continued* boiling converts all the three principles into an acid, termed *parapectic*. Pectose is supposed to have the power of transforming pectine into *pectic and pectosic acids*. These acids are also formed from pectine by the influence of an alkali or earth. Again, when these substances, which are all gelatinous, are heated, they are converted at 300° into *pyropectic acid*. Both pectic and pectosic acids are distinctly acid, gelatinous, and insoluble in cold water. The pectosic acid is first formed; it is soluble in boiling water. The pectic is insoluble in both; it also has the property of being soluble in a great number of salts, forming compounds precipitable as a jelly with alcohol. Pectosic acid is converted in pectic by long boiling; and by long boiling, renewing the water, pectic acid itself is converted into parapectic acid, which is incapable of gelatinising, very acid, and precipitates copiously salts of strontia or baryta. If the boiling is prolonged for days, the *metapectic* is formed, which does not precipitate strontia or baryta. The parapectic and metapectic acids reduce oxide of copper dissolved in alkaline fluids, but are not converted by sugar into alcohol and carbonic acid. Pyropectic acid is a brown substance, like the humus obtained from sugar. Pectose is supposed to be azotised, and the following are supposed to be the formulas of these substances, all deriving from $C_3H_5O_7$:—

| | | | | |
|---|---|---|---|---|
| Pectine | . | . | . | $C_{64}H_{40}O_{56},8HO$ |
| Parapectine | . | . | . | $C_{56}H_{40}O_{56},8HO$ |
| Metapectine | . | . | . | $C_{61}H_{40}O_{56},8HO$ |
| Pectoric acid | . | . | . | $C_{32}H_{20}O_{28},3HO$ |
| Pectic acid | . | . | . | $C_{32}H_{20}O_{28},2HO$ |
| Parapectic | . | . | . | $C_{24}H_{15}O_{21},2HO$ |
| Metapectic | . | . | . | $C_8H_5O_7,3HO$ |

*Furfurine*, $C_{30}H_{12}N_2O_6$, *Furfurole*, $C_{10}H_4O_4$.—Furfurole is prepared by distilling six parts of bran with five of sulphuric acid, diluted considerably; or by mixing two parts of bran, one of $SO_3$, and one of water, and passing over them a current of steam, collecting the product; in either case the watery product is found to contain a volatile oil, which is furfurole. This fluid is repeatedly distilled, retaining only the first part of the liquid, and at length the furfurole is the sole product. It is a clear, pale yellow, volatile oil, soluble in water, alcohol, and ether, of sp. gr. 1·650, which boils at 340°; it has a fragrant odour. When ammonia is in contact for some time with this substance, furfurolamide is formed, which is a crystalline substance of the formula $C_{30}H_{12}N_2O_6$, isomeric with furfurine; it is decomposed by boiling

water into ammonia and furfurole. When this substance is boiled with a weak solution of caustic potass, it is dissolved, and after a time, on cooling, an oil falls, from which, gradually, white silky needles of furfurine are deposited. These crystals should be purified by being boiled in a weak solution of oxalic acid, the oxalate of furfurine, which separates on cooling, boiled with animal charcoal, and the oxalic acid removed by ammonia. Furfurine is without taste or smell, insoluble in cold water, soluble in 135° of boiling water, very much so in alcohol and ether. It has very feeble alkaline reactions. It melts under 212°, and burns, when heated, with a smoky flame.

*Glycirrhizine* is obtained from a decoction of liquorice root by precipitating it, while hot, with basic acetate of lead, decomposing the precipitate with sulphuretted hydrogen, evaporating the filtered liquid, and taking up the residue with absolute alcohol; after driving off this, there remains a mass described as brown and translucent, of a sweet yet bitter taste, insoluble in ether. Liquorice owes its sweet taste not alone to this substance, but to a sugary principle which exists in the root with it.

*Meconine*, $C_{10}H_5O_4$, is obtained from the watery extract of opium. When all has been separated from this that ammonia can separate, the ammoniacal liquors are united, and evaporated to the consistence of a syrup, and then left in a cool place for from 15 to 20 days. Meconine crystallises mixed with meconates and other impurities. The crystals are then expressed, and dissolved in boiling alcohol, of which two-thirds are distilled off; the meconine crystallises afresh. It is purified by solution in boiling water, and boiling with animal charcoal. It crystallises in hexagonal prisms, terminated by a dihedral summit. It is inodorous, without taste at first, but afterwards the taste is intensely bitter. It is soluble in 265 parts of cold water, in 18·5 of boiling water, and very soluble in alcohol and ether, melts at 158°, and boils and distills without alteration. It is soluble in the caustic alkalies, muriatic and acetic acids. Nitric acid dissolves it, and converts it into nitro-meconic acid.

*Cantharidine*, $C_{12}H_6O_4$.—It is obtained by treating cantharides with ordinary alcohol, which is removed by distillation. There are obtained two layers of liquid, of which the lighter, green and oily, solidifies on cooling. This is cantharidine, which is to be purified by new solutions in alcohol. When cantharides are heated in oil of olives, the cantharidine is volatilised first, and is found in the beak of the retort. Cantharidine is colourless, inodorous, fusible, and volatile. It has all the blistering properties of the insects from which it is obtained.

*Picrotoxine*, $C_{12}H_7O_5$, is obtained by unshelling the berries of cocculus indicus, and exhausting them by alcohol; the alcohol is distilled off, and leaves behind it a fatty mass, whence the picrotoxine crystallises out. The crystals are expressed from this, re-dissolved in alcohol, and re-crystallised, after being purified by animal charcoal. It crystallises in needles. Is inodorous, but has an excessively bitter acrid taste. Heat decomposes it without melting. It requires 25

parts of boiling, and 150 parts of cold water to dissolve it. It is very soluble in alcohol and ether; insoluble in fixed and volatile oils. This is a violent poison, and has the singular property of causing an animal to walk or run backwards.

*Antiarine*, $C_{14}H_{15}O_5$, has been extracted from the *upas antia*. It is obtained by exhausting the plant with alcohol, then treating the alcoholic extract with water, which removes from it the antiarine, which crystallises from the watery solution in pearly plates. It is inodorous; when heated, it loses two equivalents of water, melts at 220°, becomes brown at 240°, and is decomposed. It is heavier than water, soluble in 250 parts of cold, and 27 of boiling water, in 70 parts of alcohol, and 2·7 of ether. Nitric and muriatic acids, and ammonia and caustic potass, dissolve it without alteration; sulphuric acid colours it brown. When introduced into wounds, it occasions instant death.

To these many others might be added, there being hardly a vegetable which does not yield some principle or other of this class, as there is hardly any which does not yield one of an alkaloidal nature.

Among the remaining principles may be enumerated—claterine, colocynthine, &c. &c. As the alkaloids referred to were quoted more as sufficient specimens of these substances than as including a complete list of them, so it is with these principles.

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## CHAP. 11.—COLOURING OR PIGMENTARY MATTERS.

Several of these principles contain a high equivalent of carbon, combined with oxygen and hydrogen.

*Madder* (*rubia tinctarom*) contains in it a colouring matter, which gives the most intense red with mordants of alum. While the plant is growing there is no trace of a red matter. It contains a yellow matter, whose colour is more deep as the age of the plant is more advanced; but as soon as the root is removed and dried in the air, this yellow matter becomes red and granular. The colouring matter of madder resists the action of concentrated sulphuric acid, while the other principles are carbonised and destroyed by it in part. When madder is exhausted by boiling alcohol, and the alcoholic tinctures, which are of a fine red, are evaporated, an extract is obtained called colorine. This is in a fine powder of an ochrey yellow, which stains the fingers, and scarcely colours the saliva. When this is gently heated, it yields a yellow vapour, which condenses in fine bright red needles, which have been called *alizarine*. To produce pure alizarine, these crystals must

be redissolved in weak alcohol, and crystallised by evaporation. Thus needle-like crystals are obtained, of an orange red, without smell or taste; very slightly soluble in cold water, a little more so in boiling water; very soluble in alcohol, which they colour red, and soluble in ether, which they colour yellow. Alizarine melts and volatilises on being heated. It yields, with ammonia, potass, and soda, solutions of a violet colour, which are precipitated blue by solutions of baryta, strontia, and lime.

By the mode in which madder is treated, different substances appear to be extracted from it. These principles, called madder purple and madder red, were formerly supposed to be, along with alizarine, sufficient to account for the colouring principle of madder. If madder is exhausted with boiling water, and the liquid filtered and precipitated by sulphuric acid, a brown substance falls, which is said to contain six substances. This is to be well washed with cold water, and then subjected to the action of boiling alcohol, by which alizarine, *rubiacine*, and *rubiane* are dissolved, with resinous matter; then alumina moist is added until the colour is removed; the colouring matter being separated by its affinity for the fresh alumina. By boiling with carbonate of potass, the other colouring matters are removed from the alumina, which, however, holds the alizarine. By boiling the compound of alizarine and alumina in muriatic acid, these are separated, the alumina dissolved, and the alizarine left, which can then be crystallised from alcohol or by sublimation. The formulas of it have been very differently given. It is certain that alizarine is the chief colouring principle; the nature of those combined with it does not appear precisely ascertained.

*Logwood.* The wood of the hæmatoxylon campechianum sometimes contains crystals of its peculiar colouring matter hæmatoxyline. This matter is easily extracted. It is only necessary to obtain a watery extract and crystallise from an alcoholic or ethereal solution of this. It crystallises in brilliant yellow needles or rhombs, which have the formula $C_{40}H_{17}O_{15}$, are slightly soluble in cold and extremely so in boiling alcohol. Nitric acid converts it into oxalic acid. Potass colours it violet. Barytes water gives a bluish white precipitate, sugar of lead a white precipitate, which soon becomes blue. *Hæmateine* is produced by the simultaneous action of ammonia and the oxygen of the air, on hæmatoxyline, or by dissolving the latter in ammonia and precipitating by acetic acid. It is a granular crystalline substance of a violet hue, with a metallic reflection. It has something of an acid character; it is said to have the formula $C_{40}H_{15}O_{15}$.

*Safflower, Carthamus Tinctorius, and its pigments.* The flowers of this plant yield a yellow and a red dye. The flowers yield to water a yellow colouring matter mixed with albumen and gum, which are to be separated by acidulating the water with acetic acid, and precipitating with acetate of lead. The liquor is then to be filtered, and ammonia added, which throws down the lead compound of the colouring matter. This is then to be decomposed by dilute sulphuric acid, the excess of the acid removed by acetate of baryta, and evaporated to a

syrup, which is to be exhausted by alcohol, the alcohol driven off, and water added to the new residue ; thus a brown precipitate is formed while the water holds dissolved the pure yellow colouring matter. In this process the contact of air must be avoided as much as possible, and the evaporating processes conducted in retorts. The watery solution is acid and bitter, and has great dyeing powers. The formula for the yellow principle is said to be $C_{24}H_{12}O_{13}$.

The red matter is obtained when the safflower which remains is treated with water containing 15 per cent of crystallised carbonate of soda in solution. The liquid is expressed, neutralised by acetic acid, and cotton is immersed in it which precipitates the red matter or carthamine. At the end of a day this is steeped in a watery solution of carbonate of soda of 5 per cent., and the carthamine is dissolved in it. Citric acid separates the flocculi of a fine crimson tint, which are to be washed with water as long as it removes salts. When these flocculi are dried they acquire a green metallic lustre. These, when dissolved, become of a deep red. Its formula is $C_{14}H_8O_7$.

*Saffron;* the coloured stigmata of the flowers furnish a dye which has been employed for some slight purposes, but is too expensive for use.

A yellow colouring matter is derived from the berries of the rhamnus tinctoria. They contain two colouring principles, which have been termed chrysorhamnine and xanthorhamnine. The former is obtained from the unripe berries by the action of ether, which leaves it on evaporation in silky crystals of a bright golden yellow. The latter is removed from the ripe berries by the action of water. It is of a deep olive yellow, and amorphous.

The colouring matter of Brazil wood is easily obtained by the action of water, and can be crystallised in orange coloured needles.

*Gentianine,* $C_{14}H_5O_5$.—Dry gentian root macerated with water yields several principles ; again dried and exhausted with alcohol it furnishes a tincture which is to be concentrated, and whose residue on the addition of water deposits brown yellow flocculi, which are gentianine in great part. These are to be collected, steeped in cold water, and expressed several times ; then all the fat removed from them by digestion in ether, and the residue dissolved in alcohol ; from which solution the gentianine crystallises in fine needles, which are insipid and inodorous, of a pale yellow colour. This substance, very slightly soluble in water, has the property of furnishing several fine colours with acids, as for instance a fine olive green with sulphuric, and a grass green with nitric acids.

Among other colouring matters may be enumerated those derived from the quercitron, sandal-wood, and rhubarb. The colouring principle of the last can be obtained crystallised.

*Indian Yellow* is a substance known under the name of *purree,* which is supposed to be an extract from the urine of the buffalo.* It is found in round masses weighing 1,500 or 1,600 grains, brown externally, and of a rich orange internally. It is soluble in water and

* This origin is doubted.

alcohol. Ether extracts from it an acid matter of a brilliant yellow colour. The alkalies dissolve a portion of *purree*, and acquire a yellow colour. When it is steeped in water, acidulated with muriatic acid, a crystalline semi-fluid mass is formed which is *euxanthic acid*, which, along with magnesia, is almost the whole constituent of the purree. This substance, slightly soluble in cold water, is soluble in boiling water, from which it crystallises in long silky faint yellowish needles. To its property of forming yellow compounds with alkalies and earths, the colour of the purree appears to be owing. When heated, euxanthic acid partly melts and partly sublimes. The sublimed portion is yellow, crystalline, slightly soluble in water, soluble in alcohol and ether. It is neutral, and has been termed *euxanthone*.

*Aloes and its colouring principle.* This principle, *aloetine*, is distinct from resins, being soluble in water and insoluble in the oils. Aloes contain 85 per cent. of it. It is obtained by concentrating the aqueous infusion, and adding to it excess of sugar of lead; aloetine remains in the fluid, which is decanted from the precipitate, and ammonia added to the filtered liquor. The aloetine is precipitated with the oxide of lead, which was in excess in the fluid as acetate of lead. This precipitate, of a consistence like thick varnish, is suspended in water, and decomposed with sulphuretted hydrogen, a liquid is obtained which, dried *in vacuo*, leaves a scaly pale yellow varnish, which is aloetine. It is soluble in water and alcohol, and slightly soluble in ether, and insoluble in fixed and volatile oils. Exposed to the air, it soon acquires a deep colour, and very small quantities of oxygen give it a deep red hue. Its formula is $C_6H_{14}O_{10}$.

*Aloeine*, $C_{34}H_{18}O_{14},HO$, is another principle also possessing colouring properties, forming a deep red solution, which has been derived from aloes. It is obtained by pounding aloes with sand, steeping in water, and evaporating the solution *in vacuo*. It is said to have slightly alkaline properties, and to possess the active power of the drug.

*Chrysammic Acid*, $C_{15}H_2N_2O_{12}HO$, is obtained by steeping 1 part of aloes in 8 of $NO_5$, sp. gr. 1·37, and heating the mass in a porcelain capsule until the chief part of the action is over, then distilling off in a retort two-thirds of the nitric acid; three or four parts of nitric acid are afresh introduced into the retort, and the whole kept for two or three days at a temperature near the boiling point. After disengagement of gas has ceased, water is added to the residue, which forms a precipitate—the chrysammic acid. The mother liquid contains oxalic and chrysolipic acids, which latter appears to be picric.

The chrysammic acid precipitated contains nitric and picric acids, from which it is freed by copious washing, and then remains a brilliant scaly powder of a yellow green colour. Dissolved again in boiling water, saturated with carbonate of potass and precipitated by nitric acid, it is in brilliant scales of a golden yellow colour, slightly soluble in cold, more soluble in boiling water, and forming a red solution of a bitter taste. It is very soluble in alcohol and ether, and in the mineral acids. It explodes when heated, and forms explosive salts, which are mostly coloured.

*Chlorophylle*, the supposed green colouring matter of leaves, exists in small quantity, is difficult to procure, and of doubtful nature.

*Cochineal.*—The insect from which the colour of carmine is derived contains, of course, like all animals, numerous principles of an albuminous, fatty, and saline character, and there was much doubt as to the nature of the colouring matter, but this now appears to be due to a principle which has been termed carminic acid. It is obtained by treating a watery decoction of cochineal with acetate of lead, and decomposing the precipitated carminate of lead with sulphuretted hydrogen; the solution in which the carminate of lead had been suspended is then evaporated to dryness, in a water bath, and dissolved in alcohol; then digesting the alcoholic solution with carminate of lead, which precipitates some phosphoric acid; then ether is added to separate some azotised matter. The fluid evaporated gives a powder of a fine brown colour, which in solution gives the beautiful hue of carmine. It is a feeble acid. With nitric acid and oxalic acid, it forms a compound which crystallises in yellow rhombic crystals, and has explosive properties. The formula of carminic acid is $C_{28}H_{14}O_{16}$.

## COLOURING PRINCIPLES OF THE LICHENS.

These plants furnish, under various treatment, several blue, purple, or red colouring principles. Litmus, archil, and cudbear, very similar colouring principles, are derived from the exposure of these plants to the air, and the action of ammonia, *i.e.*, the plants are ground and mixed in practice with putrid urine, and exposed to the air. The principal lichen used is the rocella tinctoria, from which archil is obtained, lecanora tartarea, which furnishes litmus and cudbear; but many other lichens furnish these colouring matters; and the manufactured articles owe this difference almost entirely to the mode of preparation. The chemical principles which form the colours appear to be erythric acid, the chief of these, alpharocellic, betarocellic, evernic, and parellic acids, which are derived primitively from the lichens; also lecanoric acid, and orsellinic acid, and picroerethyrine, orceine, and orcine, from the others. As the history of these substances is very complicated, and their nature by no means clear, only erythric and lecanoric acids and orceine will be described.

*Erythric Acid*, $C_{34}H_{19}O_{15},3HO$, may be prepared in at least two ways. Perhaps the easiest is to boil rocella tinctoria with milk of lime and precipitate the erythric acid by muriatic acid, and then the precipitate is to be dried, and dissolved in *warm* alcohol, from which solution erythric acid crystallises on cooling. It is colourless, slightly soluble in cold or boiling water, most soluble in ether. Boiled with water for some time, it yields picro-erythrine and orsellinic or lecanoric acid. By further boiling it is converted into orceine. Boiled with alcohol it furnishes orsellinic ether, with ammonia it gives a red colour, heated it gives a sublimate of orceine.

*Lecanoric Acid*, $C_{18}H_8O_8$, may be obtained from species of lecanora

or parelia by extracting them with alcohol and ammonia, pre-
cipitating by the addition of ammonia, and dissolving and crystal-
lising the precipitate by alcohol.    This substance is in white silky
crystals, which are very little soluble in water, most soluble in ether.

    *Orceine*, $C_{18}H_{10}NO_5$, is obtained by the action of muriatic acid on
archil.    The acid extract is evaporated, and the residue extracted by
alcohol, the alcoholic fluids are distilled, and the residue washed, there
remains a red powder very soluble in alcohol, to which it communicates
a red hue, and from which it is thrown down by water.    After the
extraction of the orceine there remains in archil an oily acid, which
has been termed erythroleic, adding another to these numerous
principles derived from the lichens, whose nature has been made to
change very often of late, so that there cannot but be great probability,
that different names have been given to the same substance, and the
same name to different substances.

    In dyeing some colours require no *mordant*, that is to say, have
the property of fixing themselves in the organic matter which they
are required to colour ; but the greater number require a mordant,
*i.e.* generally, a metallic oxide to assist them in fixing themselves in
the cloth by the attraction many of these substances have for
colouring and organic matters.    In some cases the pigmentary matter
combines with the oxide decomposing its salts ; in others, the affinity
of the colouring matter for the oxide of the salt is assisted by some
decomposing agent, salts of the oxide being used, not the oxide itself,
in order doubtless that the oxide may be in the nascent state when
it combines with the organic matter.

# ENGLISH WEIGHTS AND MEASURES.

### AVOIRDUPOIS IMPERIAL WEIGHT.

| Ton. | | Hundredweight. | | Stone. | | Pound. | | Ounce. | | Drachm. | | Grain. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | = | 20 | = | 160 | = | 2240 | | | | | | |
| | | 1 | = | 8 | = | 112 | | | | | | |
| | | | | 1 | = | 14 | | | | | | |
| | | | | | | 1 | = | 16 | = | 256 | = | 7000 |
| | | | | | | | | 1 | = | 16 | = | 437·5 |
| | | | | | | | | | | 1 | | 27·34375 |

### TROY WEIGHT.

| Pound. | | Ounce. | | Pennyweight. | | Grain. |
|---|---|---|---|---|---|---|
| 1 | = | 12 | = | 240 | = | 5760 |
| | | 1 | = | 20 | = | 480 |
| | | | | 1 | = | 24 |

### APOTHECARIES' WEIGHT.

| Pound. | | Ounce. | | Drachm. | | Scruple. | | Grain. |
|---|---|---|---|---|---|---|---|---|
| 1 | = | 12 | = | 96 | = | 288 | = | 5760 |
| | | 1 | = | 8 | = | 24 | = | 480 |
| | | | | 1 | = | 3 | = | 60 |
| | | | | | | 1 | = | 20 |

### IMPERIAL MEASURE.

| Qr. | | Bshl. | | Peck. | | Gallon. | | Quart. | | Pint. | | Cubic inch. | | Imp. lbs. | | Troy grains. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | = | 8 | = | 32 | = | 64 | = | 256 | = | 512 | = | | | 640 | | |
| | | 1 | = | 4 | = | 8 | = | 32 | = | 64 | = | | | 80 | | |
| | | | | 1 | = | 2 | = | 8 | = | 16 | = | | | 20 | | |
| | | | | | | 1 | = | 4 | = | 8 | = | 277·274 | = | 10 | = | 70,000 |
| | | | | | | | | 1 | = | 2 | = | 69·3185 | = | 2·5 | = | 17,500 |
| | | | | | | | | | | 1 | = | 34·65925 | = | 1·25 | = | 8,750 |

## FRENCH MEASURES.

| | | | |
|---|---|---|---|
| Millitre | = | *Eng. Cub. in.* ·0610 | = 16·3 min. Brit. Apoth. Meas. |
| Centilitre | = | ·6103 | = 2·705 fl. drs.　Do. |
| Decilitre | = | 6·1028 | = 3·381 fl. oz.　Do. |
| Litre | = | 61·028 | = 1·7608 Imp. Pint. |
| Decalitre | = | 610·28 | = 2·201 Imp. Gal. |
| Hectolitre | = | 6102·8 | = 22·01 Do. |
| Kilolitre | = | 61028·0 | = 27·51 Imp. Bushel. |
| Myrialitre | = | 610280·0 | = 34·39 Imp. Quarter. |

## FRENCH WEIGHTS.

| | | | |
|---|---|---|---|
| Milligramme | = | ·0154 grs. English Troy. | |
| Centigramme | = | ·1543 grs. Do. | |
| Decigramme | = | 1·5434 grs. Do. | |
| Gramme | = | 15·434 grs. Do. | |
| Decagramme | = | 154·3402 grs. | = 5·65 drs. Imp. Weight. |
| Hectogramme | = | 1543·4023 grs. | = 3·527 oz. Imp. |
| Kilogramme | = | 15434·0234 grs. | = 2·205 lbs. Imp. |
| Myriagramme | = | 154340·2344 grs. | = 22·047 lbs. Imp. |

MODE OF CONVERTING DEGREES OF THE CENTIGRADE SCALE OF THE THERMOMETER INTO DEGREES OF FAHRENHEIT.—100° of Centigrade corresponds to 212° Fahrenheit; but the Centigrade commences at 32°. A degree of the Centigrade must, therefore, be multiplied by $\frac{9}{5}$, the relation of 180° to 100, and the 32 added to the result to correct 1 of the Centigrade into Fahrenheit.

# GLOSSARY.

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Acid. *Acidum*, from 'ακη, a point.

Affinity. *Affinitas*, alliance. Used by Boerhaave to express the tendency of two different substances to combine.

Alcohol. From the Arabic, *al*, definite article, and *cohol*, antimony. Finely powdered antimony being applied to the eyelids by the Eastern women as a cosmetic, afterwards, anything reduced to the greatest degree of tenuity was said to be *alcoholised*.

Alcohol, absolute. *See* Spirit of wine.

Ammonia. From *Sal-ammoniac*, which was so called because it was procured from Ammonia, in Lybia.

Alkali. From *al*, Arabic article, and *kali*, which, according to Van Helmont, signifies ' anything burnt.'

Alkaloid. From *alkali* and ἔιδος, resemblance. A proximate principle, with properties like those of an alkali.

Analysis. 'Ανάλυσις, from 'αναλύω, to separate. An operation for determining the composition of a substance by resolving it into its constituent parts.

Anhydrous. From *a*, privative, and ὕδωρ, water. Free from combined water.

Atom. 'Ατομος, from *a*, priv., and τέμνω, to divide. An ultimate, indivisible particle of matter.

Atomic theory. A theory devised by Dr. Dalton, which regards chemical combination as taking place between the atoms of matter, and the atoms as having different weights.

Atomic weight. The weight of one element (according to a given standard) which combines with other elements.

Azote. From *a*, priv., and ζωή, life, because unfit for respiration. Nitrogen.

Boruret. A compound of *boron* with another substance.

Bromide, Bromuret, synonymous. A compound of bromine with another substance.

Caloric. *Calor*, heat. Heat considered as a material substance.

Carbide, Carburet, syn. A compound of carbon with another substance.

Carbo-hydrogen, Hydride of Carbon, Hydro-Carbon, Hydro-Carburet, syn. A compound of carbon and hydrogen.

Catalysis. Κατάλυσις, destruction. According to Berzelius, a peculiar force, which causes fermentation and all the other chemical phenomena produced by contact. Etymologically incorrect, because sometimes applied to an act of combination, at other times to one of decomposition.

CHEMISTRY. Derived by some from χέω, or χύω, to pour; but (as the art is believed to be of Ægyptian origin) more probably from Chemia, the ancient name of Ægypt in the sacred language of the priests.

CHLORIDE, CHLORURET, syn. A compound of chlorine with another substance.

CHLORINE. From χλωρὸς, yellowish green, on account of its colour.

CHOKE-DAMP. From the German, dampf, vapour. A name given by miners to carbonic acid. See FIRE-DAMP.

COLOPHONY. From Κολοφων, a city in Ionia, whence it was first brought. The resin which remains after distilling turpentine without water.

COPPERAS. Couperose, Fr. Sulphate of iron. Sometimes called green vitriol.

CREASOTE. From κρέας, flesh, and σώζω, to preserve. So called on account of its antiseptic property.

CRYSTAL. Κρύσταλλος, ice. A body of a regular geometrical figure, formed by the solidification of a liquid, or gas.

CUPELLATION. A process of purifying metals by melting them with lead in a cup made of phosphate of lime.

DECANTATION. The process of pouring off a fluid from solid particles which have subsided to the bottom of the vessel.

DECOMPOSITION. From de, and compono, to put together. The separation of bodies chemically combined together.

DECREPITATION. From de, and crepito, to crackle. The crackling noise produced when certain bodies, especially salts, are exposed to heat.

DEFLAGRATION. In a more extended sense, every process of decomposition attended with noise or detonation. In a restricted sense, it signifies the oxidation of a substance in the dry way (at the expense of the oxygen of another admixed substance), attended with combustion and noise, or detonation.

DIGEST. From digero, to separate. To steep for some time in a liquid maintained at an elevated temperature.

DISTILLATE. The fluid reproduced in the process of distillation.

DISTILLATION. An operation which serves to separate a volatile liquid from a less volatile or fixed substance, and subsequently to recover the evaporated fluid. The apparatus consists essentially of three parts. 1st. A vessel in which the substance to be distilled is vaporised. 2nd. An apparatus in which the vapour is condensed. 3rd. A receiver for the condensed fluid. See EVAPORATION, IGNITION, SUBLIMATION.

DUCTILITY. Ductilis, easy to be drawn. The property of metals which renders them capable of being drawn into wires.

DUTCH LIQUID. A liquid of an oily consistence, formed by the combination of olefiant gas and chlorine. Also called Chloride of olefiant gas, and Chloric æther.

EDULCORATION. The affusion of water to remove soluble matter from any substance.

ELUTRIATION. Eluo, to wash out. The separation of the finer part of a sediment diffused through a liquid from the coarser, by pouring it off into another vessel.

EMPIRICAL FORMULA. See FORMULA.

EMPYREUMA. From Ἐμπυρένω, to kindle. The burnt smell contracted by some substances when heated without the free access of air.

EPSOM SALTS. Sulphate of Magnesia, which was formerly obtained from a mineral spring at Epsom, in Surrey.

EQUIVALENT. Used synonymously with *atom, atomic weight*, and *combining proportion*. Molecules replace each other in combination according to their atomic weights, and thence are relatively termed equivalents.

EREMACAUSIS. From Ἐρημος, solitary, and καίω, to burn. Liebig applies this term to the process commonly called *decay*, which is one of *slow combustion* by direct union with oxygen.

ESSENCE, ESSENTIAL OIL. Volatile oil obtained by the distillation of vegetables, and having, in most cases, the concentrated odour of the plant.

ETHER, CHLORIC. *See* Dutch Liquid.

ETHER, ÆTHER. From αιθηρ, pure air. Oxide of Ethyle.

ETHYL, ETHYLE. A compound radical ($C_4H_5$). With one equivalent of oxygen it forms ether (oxide of ethyle), which, with an equivalent of combined water, becomes alcohol ($C_4H_5O + HO$). *See* METHYL.

EUDIOMETRY. From Ευδια, purity of air, and Μέτρον, a measure. The art of measuring the quantity of oxygen in a given bulk of air.

EVAPORATION. By this operation volatile fluids are separated from less volatile or from fixed bodies, in cases where the residuary matter alone is of importance. *See* DISTILLATION, IGNITION, and SUBLIMATION.

FERMENT. *Fermentum*, leaven. According to Liebig, a compound in a state of progressive change, capable of setting in motion, and thereby decomposing the particles of other compounds of unstable equilibrium.

FILTRATE. The liquid which passes through a filter.

FILTRATION. The operation of passing a fluid through a porous medium in order to remove mechanically suspended solid particles.

FIRE-DAMP. A name given by miners to light carburetted hydrogen, which takes fire, as distinguished from choke-damp (carbonic acid), which kills by suffocation.

FORMULA. Diminutive of *Forma*, a form or scheme. A plan for exhibiting the composition of a substance by means of chemical symbols. A formula is EMPIRICAL when it simply denotes the constituents in their relative proportion, as ether, $C_4H_5O$; and RATIONAL when it signifies the probable mode in which the atoms are arranged. Thus ether may be regarded as oxide of ethyle, or $C_4H_5 + O$.

GAS. From *Geist*, spirit, Germ. A name of which Van Helmont claims the introduction. In the key to his works it is described as "spiritus seu exbalatio sylvestris, quæ nec coerceri nec coagulari valet," &c.

GLAUBER'S SALT. Sulphate of soda.

GRAVITY. The absolute weight of a body without reference to its volume.

GRAVITY, SPECIFIC. The relative weight of a body, volume for volume, as compared with some standard which serves as a unit. Pure water is used as the standard of comparison for solids and liquids, and atmospheric air for gases.

GYPSUM. Γύψος, from γη, earth, and ἐψω, to boil. Sulphate of lime heated till nearly anhydrous, and then reduced to powder. It becomes *Plaster of Paris* on the addition of water.

HALOID. From ῎Αλς, sea salt, and ῎ειδος, resemblance. Applied to salts which resemble sea salt in their composition.

HARTSHORN, SPIRIT OF. SALT OF. An ammoniacal liquor and crystalline salt, obtained by the destructive distillation of stags' horns. The names are retained in common speech for aqua ammoniæ and sesquicarbonate of ammonia.

HERMETIC SEALING. From ῾Ερμες, Mercury, the father of chemistry. The closing of a glass vessel while in a state of fusion.

HYDRATE. From ῎Υδωρ, water. A substance containing chemically combined water.

HYDRIDE, HYDROGURET, HYDRURET. A compound of hydrogen with another substance.

HYPER. ῎Υπερ, above. Prefixed to the names of acids, denotes that they contain more oxygen than the name indicates without the prefix.

HYPO. ῎Υπο, under. In composition, the converse of hyper.

IGNITION. The operation of exposing solid substances to a strong heat in a crucible, and serving in some measure for solids the same purpose as evaporation with regard to liquids. In some instances, however, substances are ignited simply for the purpose of modifying their state without any volatilisation taking place. *See* DISTILLATION, EVAPORATION, SUBLIMATION.

INFUSE. To steep a substance in a liquid, with or without heat, in order to dissolve out the soluble matter.

IODIDE, IODURET. A compound of iodine with another substance.

ISOMERIC, ISOMERISM. From ᾽Ισος, equal, and μέρος, a part. Applied by Berzelius to bodies having the same composition, but different properties.

ISOMORPHOUS, ISOMORPHISM. From ᾽Ισος, equal, and μορφὴ, form. Terms devised by Mitscherlich to express similarity of crystalline form with diversity of elementary constitution.

LEVIGATION. From *Lævigo*, to make smooth. The reduction of a substance to powder by rubbing it when made into a paste with water. *See* TRITURATION.

LUNAR CAUSTIC. From *Luna*, the alchemical name for silver. Nitrate of silver.

MACERATE. From *Macero*, to make soft by steeping. To steep a substance for an indefinite time in a liquid, whether with or without heat, in order to soften it.

MALLEABILITY. From *Malleus*, a hammer. The property possessed by certain metals of being extensible into thin plates by hammering.

MENSTRUUM. From *Menstruus*, monthly. A solvent. The name is probably derived from some notion of the old chemists about the influence of the moon on the action of solvents.

METHYL, METHYLE. A compound radical ($C_2H_3$). With oxygen it forms an oxide ($C_2H_3O$), analogous to ether; and with the further addition of water ($C_2H_3O + HO$) it constitutes *pyroxylic spirit* or *medicinal naphtha*, analogous to alcohol. *See* ETHYL.

METALLURGY. Μεταλλον, and εργον, work. The part of chemistry which relates to the treatment of metals.

MICROCOSMIC SALT. From *Microcosm*, or little world, a fanciful

designation for the human body. Phosphate of soda and ammonia, which exists in the urine.

MOTHER WATER. The liquor which remains after the separation of a substance by crystallisation.

MURIATIC ACID. A compound of one atom of chlorine and one of hydrogen. Hydrochloric acid.

MURIATIC ACID, OXYGENATED. OXYMURIATIC ACID. Names formerly given to chlorine when regarded as a compound of muriatic acid and oxygen.

NAPHTHA. Νάφθα, Gr. 1. A native bituminous liquid, having the composition $C_6H_5$. 2. A name improperly applied to pyroxylic spirit.

NATRON. A name of obscure derivation, formerly given to carbonate of soda. The two initial letters (Na) furnish the chemical symbol for sodium.

ŒNANTHIC ACID, ŒNANTHIC ETHER. From οἶνος, wine, and ἄνθος, a flower. Œnanthic acid is found in wine and some other fermented liquors, combined with ether (oxide of ethyle), forming œnanthic ether, or œnanthate of oxide of ethyle. This ether is the cause of the peculiar odour of wine.

OSMAZOME. From Ὀσμή, odour, and ζωμός, broth. A name given by Thenard to an extract of flesh, supposed to be the source of the odour and flavour of dressed meat; but later researches have shown that it is a mixture of different substances.

PETROLEUM. From *petra*, a rock, and *oleum*, oil. Rock oil. Barbadoes tar. A species of bitumen of the consistence of a thick fluid, found in England, but chiefly in Barbadoes, Trinidad, Rangoon, and other places.

PRECIPITATION. From *præcipito*, to cast down. The sudden conversion of a substance held in solution into the solid state by the addition of a *precipitant*, which latter may act either by modifying the solvent power of the menstruum, or by a chemical change in the deposited matter.

PROXIMATE PRINCIPLE. An organic substance in its simplest form, or that which approaches nearest to resolution into its ultimate elements.

PROTEIN, PROTEINE. From Πρωτεύω, to be first. A hypothetical radical, supposed by Mulder to be the basis of the albuminous or sanguigenous compounds.

PRUSSIC ACID. A name of hydrocyanic acid, because it was first obtained from Prussian, or Berlin, blue. This was by Scheele, in 1782.

PUTREFACTION. A kind of eremacausis, differing from the ordinary kind in the offensive odour of some of the products, chiefly sulphuretted and phosphuretted hydrogen.

RATIONAL FORMULA. *See* FORMULA.

REAGENTS. Substances which indicate the presence of others by any striking phenomena. Tests.

RECEIVER. In distillation, that part of the apparatus which receives the condensed vapour. *See* DISTILLATION.

RECTIFICATION. The process of purifying by a second distillation.

REDUCTION. The operation of restoring a metal when in composition to the metallic state.

RESIN. From Ῥέω, to flow, because it flows spontaneously from the

tree. A compound generally associated with an essential oil, insoluble in water, soluble in alcohol, and very inflammable.

RETORT. From *Retorqueo*, to turn back. A chemical vessel with a neck bent to an angle with the body. When provided with a tubular opening in the roof, to be fitted by a stopper, it is said to be *tubulated*.

ROASTING. A process generally performed in a crucible, by which minerals are heated preparatory to other operations.

ROCHELLE SALT. SEIGNETTES SALT, syn. Tartrate of potash and soda.

SALT-PETRE. From *sal*, salt, and *petra*, a rock. Nitrate of potash.

SOAP. From *Sapo*, Lat. A compound in definite proportions of certain principles in oils, fats, or resins, with a salifiable base. Plasters are soaps of certain metallic oxides.

SATURATION. 1. The state of a fluid in which it has dissolved as much as it can of another substance. 2. When two principles are united in such proportion that neither predominates, they are said to saturate one another.

SCHEELE'S GREEN. Arsenite of copper.

SOLUTION. In its widest sense, this includes the perfect union of a fluid with any substance whether gaseous, liquid, or solid. But the first is more properly *absorption*, and the second *mixture*. In general, the term is restricted to the perfect union of a *solid* substance with a fluid.

SPIRIT, ARDENT. The produce of the distillation of a fluid which has undergone the vinous fermentation.

SPIRIT, PROOF. Spirit of the density, as fixed by law, of 0·920°.

SPIRIT OF WINE. The first produce of the distillation of ardent spirit. When re-distilled, it is called *rectified spirit of wine*. This contains from 10 to 20 per cent. of water, which may be removed by adding dry chloride of calcium, carbonate of potash, or lime, and re-distilling. It now has a density at 60 F. of about 0.795,° and is called *pure*, or *absolute alcohol*. A mixture of alcohol and water, of density 0·920° is called *proof spirit*.

SUBLIMATE. A substance volatilised and re-condensed by the process of Sublimation.

SUBLIMATION. A process which serves to expand solid bodies into vapour by the aid of heat, and, subsequently, to re-condense the vapour to the solid state by refrigeration. Sublimation is, consequently, *a distillation of solid bodies*. *See* DISTILLATION, EVAPORATION, IGNITION.

TEST. Any re-agent, which, added to a substance, teaches us to discover its chemical nature in composition.

TRITURATION. The process of comminuting by friction without the intervention of a liquid. *See* LEVIGATION.

VITRIOL. (Supposed to be derived from *vitrum*, glass, from its resemblance to glass.) Three metallic sulphates are known by this name. 1. White vitriol, or sulphate of zinc. 2. Blue vitriol, or sulphate of copper; and 3. Green vitriol, or sulphate of iron.

VITRIOL, OIL OF. Sulphuric acid; so called because obtained from green vitriol, and from its oily appearance, and its soapy feel between the fingers.

# INDEX.

# CORRIGENDA.

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Page 9—for "Tangeten" read "*Tungsten.*"

Page 136—for "HgBr2" read "HgBr."

Same page—for "HgC$_3$" read "HgCy."

Page 153, line 16 from bottom, after "silver," insert "to the water, after addition of a few drops of nitric or muriatic acid."

Same page, line 4 from bottom, omit "washing."

Page 225, 11th line from top—for "urea" read "*uric acid.*"

" . . . . whilst at the same time he deduces conclusions which cannot, except by similar inquiries, be refuted; hence the value of a practical work of this description, which must stand the test of time."—*Edinburgh Medical and Surgical Journal, April* 1, 1847.

" Further, the work contains original investigations into the pathology of the disease, which were commenced in a right spirit, and under the guidance of sound principles. The microscope and chemical analysis have been used freely by him, the use of which he triumphantly defends. . . . . In the discussion of the etiology of scrofula, we again find our views corroborated by Dr. Glover. He states truly, and with great candour, that Mr. Phillips's work contains by far the best account of the etiology of scrofula yet given to the world. We are bound, however, to say, that highly as we have estimated Mr. Phillips's work, we think Dr. Glover has discussed certain points in the etiology with even more philosophical precision than Mr. Phillips. . . . . We feel we ought to congratulate Dr. Glover on the able manner in which he has handled his subject."—*British and Foreign Medical Review, April,* 1847.

" . . . . while we are happy to be able to say that the work of Dr. Glover is well calculated to add weight to the more reasonable views of former writers on the subject, and also to direct the course of future inquiry. Dr. Glover's treatise is principally composed of carefully selected and arranged passages from the works of previous writers on scrofula; to which are appended brief, but comprehensive remarks, elicited by the author's own reasonings and experience of the subject, together with the results of a very considerable number of original chemical experiments and clinical investigations. . . . . Upon the whole, it is long since we have read a more carefully-written work, or one less encumbered by unnecessary details. . . . . We cordially recommend its perusal to our readers."—*Medical Gazette, April* 9, 1847.

" As we always anticipated, the medical press universally, we believe, has spoken of Dr. Glover's work on scrofula in the highest terms; and we feel assured that the profession will be pleased and instructed by its careful perusal. . . . . The brief analysis offered of the first and second chapters of this excellent work will suffice, we trust, to convince our readers of the extremely careful manner in which the author has examined each point of interest. . . . . The work does much credit to author and publisher, and cannot fail to be always esteemed, whatever discoveries may hereafter be made on the nature and treatment of this terrible malady. We, with every confidence, recommend this philosophic and original work to the most favourable notice of the profession."—*Medical Times, May* 29, 1847.

" Dr. Glover gives a concise, and, at the same time, comprehensive, statement of the results arrived at by his fellow-labourers in this most interesting field, together with those of his own carefully-conducted investigations and experiments, which entitle him to the greatest credit both for impartiality and candour. . . . . We must now conclude this notice of a most interesting work. In doing so, we congratulate the author on the manner in which he has performed his task, and cordially recommend it to our professional brethren."— *Provincial Med. and Surg. Journal, May* 5, 1847

" The whole subject has been studied attentively by Dr. Glover, and the result is a sound and practical application of his knowledge to the treatment of this important disease."—*Braithwaite's Retrospect, June,* 1847.

" Dr. Glover, in his very admirable essay on scrofula."—*Madden on Pulmonary Consumption.*

See also the numerous and very complimentary References to this Work in the last number of Copland's Dictionary—Article, " Scrofula and Tubercle."